VOLATILE SOLVENTS AND THINNERS

UNIFORM WITH THIS VOLUME

CELLULOSE ESTER VARNISHES

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VOLATILE SOLVENTS AND THINNERS

Used in the Paint & Varnish Industries

BY

NOËL HEATON, B.Sc.

PREFACE

WHEN the General Editor invited me to write this volume for the series of handbooks of which it forms a unit, I felt that one must have a good excuse before adding to the ever-increasing stream of technical publications; it is a constant source of wonder how readers can find time to cope with them.

The excuse I offer is that there is no other work in the English language which brings together for reference and comparison detailed information as to the nature, preparation and properties of every solvent of industrial importance in the paint and allied industries. Whether this will justify the book, it is for the reader to say.

To establish the limitations of my task I define a volatile solvent as an organic liquid which can be distilled without decomposition, which is capable of complete evaporation at atmospheric temperatures and which has a pronounced solvent action on oils, fats, waxes and similar substances without altering their chemical composition. This definitely excludes the less volatile compounds used as plasticisers, as well as the vegetable oils.

Whilst the work was in preparation the centenary of the discovery of benzene by Faraday was celebrated (June 16th, 1925). Of the sixty-odd substances here described only three were in industrial use before his time. When the sun first shone in the twentieth century the number in general use could be counted on the fingers, and within the past ten years the number available has been almost doubled. Whilst, therefore, much that is said about the old-established solvents is condensed from what has been said already, my daily experience of inquiries for information leads me to hope that an account of the more recent additions to the list will be welcomed. Most of such information I have obtained at first hand. It is not always possible to indicate clearly where personal experience is supplemented by statements derived from current technical literature without detracting from the " readability " of a book, but no important statement derived from published researches has been made without due acknowledgment. I have not hesitated to express my personal views on some points where opinions differ, but in doing so I have endeavoured to distinguish such individual opinions clearly from generally accepted views.

As regards the analysis of solvents, I have taken the line of excluding detailed description of apparatus and methods as readily accessible in works on analysis, indicating briefly important tests

for purity in addition to the physical properties on whic
identification of a solvent mainly depends.

In the last chapter I have outlined some of the theoi
considerations involved in the use of solvents. Full disci
of such points would be out of place in a handbook for g<
use, and these brief observations will have served their pι
if they indicate some of the problems confronting the paint
nologist and emphasise the need for realisation of that dreε
every progressive paint chemist—an organisation for syste
research on paint technology.

It is impossible to acknowledge adequately the willing res
I have met with from so many whose assistance I have soug
verifying my data; I must acknowledge, however, that throuȝ
the preparation of the work I have received constant advice
assistance from Mr. W. H. Thorns and Mr. W. Passmore.
addition, they have undertaken the irksome task, so invalι
to the author, of checking over the manuscript and suggesting ι
improvements.

It is futile to attempt literary style in dealing with massι
uninspiring technical data, where accuracy in statement of
is the primary consideration, but I have endeavoured to a
the temptation to utilise technical terms as stepping stonε
difficult points, and to give the facts, as I understand them, iι
simplest and fewest words.

NOËL HEATO

Savage Club,
  Adelphi, W.C.,
    October 1925.

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APPENDIX

VOLATILE SOLVENTS AND THINNERS

is fully saturated with hydrogen and which are therefor
stable compounds comparatively inert to chemical action.
on this account that they are known as the paraffin serie∙
parum affinis, little affinity.) The paraffins from CH_4 to
have been identified in petroleum, the most important m∙
being the group from C_5H_{12} to $C_{15}H_{32}$. The unsaturated
and naphthene hydrocarbons are also found and hydrocarb
the benzene series are present to a less extent. The numb∙
relative proportions of this large range of hydrocarbons ∙
varies enormously in the oils obtained in different parts
world. Thus American petroleum is particularly rich in pa
and olefines and contains very little of the aromatic series,
the oil obtained in Roumania contains a much larger propor∙
these benzene hydrocarbons. The content of sulphur deriv
and other impurities also varies very considerably and the
position of the oil in this respect materially affects its tec
value.

By distillation of the crude oil it can be split up into a nu
of fractions containing groups of hydrocarbons of varying b
points, ranging from volatile spirits to solid waxes. From
again by further fractional distillation a wide range of p∙
products is obtained. The first refining of the crude oil is c∙
out at the oil wells, where the oil is subjected to a prelim
distillation and separated into three portions :—

 Tops—consisting mainly of highly volatile spirits.
 Middles—containing the solvents and light oils.
 Bottoms—containing the non-volatile oils and waxes.

These semi-crude products are shipped to the various oil refi∙
concerned in the production of motor spirits, solvent spirits
burning and lubricating oils respectively. The nomenclatu∙
the various refined products obtained, most of which are stil
definite chemical compounds, but a mixture of several hydrocar
of closely approximating boiling points, is in a state of conside∙
confusion owing to the fact that as the industry developed distil
of closely similar character have attained industrial import
under a variety of different names in different industries.

In the early days of petroleum, its chief importance was a∙
illuminant, taking the place of colza and other oils at a time ∙
gas was in its infancy and electric light was practically unkn∙
Its rapid adoption for this purpose led to its practically exclu
use as a lamp oil, under the names coal oil, kerosene, paraffin

naphtha. For this purpose a slowly volatile oil is essential, as the highly volatile hydrocarbons burn too quickly and are dangerously inflammable. The volatile portions of the petroleum were therefore removed in the refining of paraffin, and these became a cheap by-product with its rapid increase in consumption.

It is now about a quarter of a century since experiments in the utilisation of this by-product resulted in its adoption as a fuel for internal combustion engines under the name of " gasolene," which rendered possible the development of the motor-car industry of to-day. The name gasolene is still generally retained in the United States, although petrol has now become the recognised name for this fraction in this country. With the growth of the motor car the demand for this highly volatile distillate left a surplus of the less volatile spirits—too volatile to be retained with safety in lamp oils, but not sufficiently volatile for the rapid vaporisation required in a motor spirit. This was available at a very low price and was introduced into the paint industry as a cheap substitute for turpentine under the names " benzoline," " benzine " and " petroleum spirit." It is only within the past few years that this product has become standardised as a recognised product and taken a definite place in the industry under the accepted name of " white spirit."

The following is a general classification of the various petroleum distillates and the approximate proportion in which they are contained in the crude oil :—

Petrol and volatile spirits about	20 per cent.	Boiling point	0° to 150°.
White spirit	,,	5 ,, ,,	,,	,,	150° to 200°.
Burning oils	,,	30 ,, ,,	,,	,,	200° to 300°.
Lubricating and fuel oils	,,	35 ,, ,,	,,	,,	300° to 350°.
Paraffin waxes } Pitch and coke }	,,	10 ,, ,,

The proportions given must only be regarded as the roughest approximation; the relative amounts of the various constituents vary enormously in different oils, even those from wells in the same district showing very considerable differences.

The proportions of different fractions obtained from the crude oil can be varied and adjusted within limits to suit the demand of the market by the process of " cracking " in which the oil is heated to break down the more complex hydrocarbons and increase the percentage of lower and more volatile hydrocarbons contained in motor spirit, etc. This treatment is accompanied by hydrogenation, to prevent the formation of the unsaturated hydrocarbons which would cause the development of a strong unpleasant odour in the product.

The specific gravity of the crude petroleum varies widely ow
to this indefinite composition.   The following are the highest :
lowest figures recorded for the specific gravity of oils from s(
of the principal districts, taken from a large range of determinati
by different observers :—

Source.	Lowest.	Highest.
Borneo	0·924	0·965
Russia	0·873	0·936
Roumania	0·801	0·926
Galicia	0·798	0·881
Persia	0·777	1·0
W. Virginia	0·798	0·825
Pennsylvania	0·771	0·828

Petrol, or Gasolene.

The crude material for this is the " tops " of the prelimin
refining of crude petroleum—the portion coming off below 16(
This is refined in the manner described more fully below (see Wl
Spirit) and re-distilled by steam under atmospheric pressure
remove any higher boiling fractions carried over in the ini
separation, which are passed over to the " middles " for product
of white spirit.   In distilleries which produce different grades
petroleum distillates, the petrol is refined in an entirely separ
plant from the white spirit and heavier grades, as more string
precautions need to be taken to avoid fire and explosion risk ow
to its low flash point.   Thus, whilst distillation under partial vacu
can be used for the heavier grades, this is not permissible for
light fractions, and the stills are arranged at a distance from
steam-raising plant, with a clear open space between them and
buildings to minimise fire risk.

The refined volatile spirit produced in this section has a w
distillation range.   The exact range and the proportion of higl
and lower fractions varies in different grades and qualities of
spirit produced by different makers.   The purest aviation spi
required by the Air Board is specified [2] to distil 10 per cent. bel
74°, 65 per cent. below 100°, and must be completely distill
below 150°.   Ordinary commercial petrol, No. 1 grade, should dis
40 per cent. below 100° and all over at 185°.   The cheaper No.
grade only shows 20 per cent. below 100° and is not complete

* All temperatures, unless otherwise stated, are expressed on the Cen
grade scale.

distilled until 200°. The specific gravity ranges from 0·725 to 0·745, varying according to the source of supply, as some petroleums show a higher specific gravity in proportion to the boiling point than others.

The predominant use of petrol is as a motor spirit, but it is also used to a certain extent as a solvent. It is not so good a solvent for most purposes as the equally volatile benzol obtained from coal tar, but it is useful for the preparation of certain types of enamels where rapid evaporation is desired and the pungent smell of benzol is objected to. It is also used to a certain extent as a solvent for rubber.

By further distillation with efficient dephlegmators, petrol is still further refined into fractions with a very close boiling range of any desired volatility, which are used for numerous industrial purposes where a boiling point within a definite range and complete absence of high boiling residual is essential. The nomenclature of these refined volatile fractions is not very closely defined and confusion is caused by the use of the same name for different fractions and *vice versa*. The following may be regarded as an approximate classification :—

Cymogene or *Rhigolene*.—This is the most volatile fraction obtainable, consisting mainly of tetrane or butane (C_4H_{10}), comprising all the distillate which boils below 0°. It is used chiefly as an anaesthetic and freezing agent.

Pentane— is a specially purified fraction consisting of almost pure normal and iso-pentane (C_5H_{12}) with a boiling range between 20° and 40° and specific gravity 0·625. It is prepared industrially on a limited scale for special purposes. The standard Pentane Lamp designed by Harcourt for photometric work may be mentioned as an example.

Petroleum Ether—consists mainly of hexane (C_6H_{14}) and heptane (C_7H_{16}) with a boiling point below 60° and specific gravity below 0·670. It is used as an alternative to ether as an analytical extracting agent for oils and fats and similar purposes.

Petroleum Spirit—the fraction coming over between 60° and 100° consisting of a mixture of about 75 per cent. paraffin hydrocarbons, chiefly hexane and heptane, the remainder being mainly olefines with a small and varying amount of aromatic hydrocarbons depending on the source from which it is obtained. The specific gravity is about 0·700. It is liable to contain

impurities in the shape of traces of heavy hydrocarbons
sulphur derivatives. The British Pharmacopœia de
petroleum spirit as a petroleum distillate boiling between
and 60° with a specific gravity between 0·670 to 0·700.
name petroleum spirit is, in fact, very loosely defined an
used by some authorities to denote a particular fraction, w
others employ it as a generic term for any volatile petro
distillate, including both petrol and white spirit.

Ligroin—is an old and obsolescent name practically syn
mous with petroleum spirit; it is generally used to imp
distillate rather heavier than petroleum spirit, but is
loosely defined.*

Mineral Naptha—is a rather heavier grade of petrol
spirit approximating to paraffin. The mineral naphtha aut
ised for use as a denaturant in the preparation of methyl
spirit must have a specific gravity ranging between 0·800
0·830.

Benzoline—is a name originally applied to any light petrol
boiling between 65° and 150°. The use of this term'fo
petroleum product is particularly confusing owing to
similarity to benzol and it might well be regarded as obso

Benzine—is the name generally applied to a re-distilled
purified petroleum spirit, free from sulphur and other impuri
which evaporates completely without leaving any trace
residual. It is used largely as an extraction and clean
agent in many industries, such as the degreasing of text
dry cleaning of fabrics, the refining of glue and gelatine,
purification of foodstuffs, the grinding to impalpable pow
of materials acted upon by water, and similar purposes.
such cases it is of importance that the solvent used should
entirely without any action on the material treated and
appear completely on evaporation, leaving the material perfe
dry without a trace of greasiness or odour. By careful fi
tionation the distillers produce benzine to any specified boil
range between 60° and 120° to suit the particular purpose
which it is to be used. Thus in degreasing, a range betw
80° and 110° is required. The inclusion of fractions bel
80° would entail excessive loss by evaporation and increa
fire risk, whilst any residual boiling above 110° would

* The author has tried without success to trace the origin of this nan
The earliest reference to it that can be found appears in Wagner's *Jah.
berichte*, Vol. XI., 1865, where mention is made of its use in a petrolo
gas lamp.

difficult to expel completely from the finished product by heating to temperatures below the boiling point of water.

Benzine is used in the rubber industry as a thinner for sulphur chloride in the cold cure process, to replace carbon bisulphide. For this purpose purity is essential, particularly freedom from olefines, which react with the sulphur chloride to form a resinous mass which is highly objectionable in the rubber. The present writer would hazard the suggestion that the name " benzine," on account of its liability to confusion with benzene, might well be abolished entirely and the name petroleum spirit possibly standardised for this purpose, qualified by a statement of the boiling range. Thus " petroleum spirit 80°—110° " would imply the particular grade described above, and so on.

White Spirit.

The first to recognise the possibilities of petroleum distillate as a solvent in the paint industry appears to have been Samuel Banner, who introduced it as Patent Turpentine in 1885.[3] For many years this was regarded as a cheap adulterant for turpentine and generally known as " turpentine substitute." As its use developed, however, and its technical possibilities and limitations became more fully investigated, it gradually attained recognition as a distinct solvent, and definite requirements as to its properties were established. As it attained a more and more definite place in industry the special name " white spirit " became gradually associated with the particular petroleum distillate which was found to answer the requirements of the paint and varnish industries as a solvent and thinner, to distinguish it from the less closely defined terms " petroleum spirit," " benzine," etc., under which one finds it generally described in publications up to about twelve years ago, and during the past few years this name has come into general use. Although the name might equally well be applied to any colourless spirit and does not convey its petroleum origin, it has the advantage of being quite distinctive and not liable to cause confusion and may be accepted as the standard title for this particular solvent. The name does not appear to have obtained currency in the United States, where the term Mineral Thinners is generally used to include all the petroleum solvents. Thus the Bureau of Standards gives the title " Volatile Mineral Spirits for Thinning Paints " to its specification (see p. 30), which is practically identical with the B.E.S.A. specification for white spirit. The name " white

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spirit " occurs occasionally in German publications, but " li
benzin " is more generally employed. The name " white spin
has been adopted in France, but Eugène Sauvage has recent
protested against its general adoption on the grounds that it is
sufficiently distinctive, and proposed that it should be replaced
" essence vernis " (varnish spirit), qualified by the description li
middle and heavy, according to the specific gravity and boi
range. To the present writer this appears to be rather a retrogr
step as not only equally lacking in precision but actually mislead
It implies that this solvent finds its chief use in the preparatio
varnishes, whereas it is of value for a large variety of other purpo
and it is perhaps as a thinner for higher-grade varnishes that
inferiority to other solvents is most marked.

Manufacture.—The raw material for white spirit is the mi
portion obtained in the preliminary refinement of petroleum, in
mediate between the light motor spirits and the burning ,
lubricating oils. This semi-refined oil is produced at the wells ,
exported to the distilleries, where it is stored in tanks ready
treatment. In common with all petroleum products, white sp
is of extremely complex composition, which varies widely accord
to the source of the crude oil and the method of refining. T
American petroleum consists, as has been shown, almost entir
of hydrocarbons of the paraffin series, whilst other petrolei
contain a varying proportion of the aromatic hydrocarbons.

As the white spirit manufacturer is concerned chiefly to prod
a satisfactory article for use as a solvent, a great deal depends
the first instance on the choice of his raw material, the chief p
to consider being to obtain an oil containing the highest poss
content of the aromatic series, which have a greater solvent po
than the paraffin series. Another point to consider in select
the semi-crude oil for the production of white spirit is the cont
of sulphur compounds and unsaturated hydrocarbons of the ole
series which give an objectionable smell to the product. At
time large quantities of high-grade white spirit were produced fr
Borneo petroleum. This formed a very satisfactory spirit, valu
to the paint industry because of the abnormally high proportio
aromatic compounds and consequent high solvent power.
fortunately, this source of supply is no longer available and Bor
spirit has not been on the market in this country for some ye
the output from Borneo at the present time being entirely absor
on the Continent. The best white spirit now available is m
from the Roumanian oil, which contains approximately 30 to 35

cent. of aromatic hydrocarbons and is remarkably free from olefines and sulphur compounds. American oil is distinctly inferior to this both in solvent power and odour. Other Eastern oils such as Persian are also used for the manufacture of white spirit, but the Southern Russian oil from Baku is useless for the purpose, particularly on account of its odour.

Starting with the semi-refined oil delivered from the wells, this is first treated to remove impurities. The chief of these are thiophenes and other sulphur compounds, which are very objectionable in the finished product, and unsaturated hydrocarbons of the olefine series. The complete removal of both these classes of impurities is essential to a first-class, sweet-smelling product.

Various processes of purification have been used at different times, such as treatment with fuller's earth. This method, in common with many others, is now obsolete, the general practice being to scrub alternately with sulphuric acid, soda and water. The sulphuric acid combines with the various impurities, forming sulphonic compounds, which separate out as a heavy, viscous mass. This operation is carried out in lead-lined tanks fitted with agitating gear and baffle-plates so designed as to ensure thorough mixing of the acid and spirit with a minimum of power. When the action is completed the tank is left to stand for the foots and water to settle out. This is then drawn off from a cock at the base of the tank and a solution of soda run into the tank to neutralise any residual acid. A final washing is given with plain water and the purified spirit is then discharged into stills fitted with steam coils. Here it is heated by steam at a pressure of about 110 lb., superheated to about 540° F. and distilled off under reduced pressure.

By careful regulation of the temperature of the steam and the vacuum the distillate is separated into fractions of different boiling range. In order to render this separation more complete the vapour coming from the still passes first through a fractionating column, consisting of a cast-iron cylinder fitted with loose baffle-plates, which act in a similar manner to the bulbs of a Glinsky fractionating column, putting on a slight back pressure. From the fractionating column the vapour next passes through a dephlegmator, the design of which varies in different works, but generally consists of a vertical steel cylinder in which are fitted a number of copper tubes through which a flow of water is maintained. The vapour from the fractionating column passes round these tubes and any portion of the distillate boiling above the required limit is condensed and returned to the fractionating column by means of a return pipe in the bottom

of the dephlegmator. This pipe is fitted with a ∪-shaped b which acts as a seal to prevent the vapour passing in the rev direction.

From the dephlegmator the vapour passes into condenser: the usual type consisting of coils immersed in a tank through wl a steady stream of cold water is circulated. The condensed lic coming from the condensers is discharged into a receiver. Tl fractions are re-distilled to produce a series of final products hav a boiling point over a definite range, from which a spirit can produced to meet any required specification.

The preliminary separation of the crude oil into the tl principal grades referred to above is inevitably imperfect, a cer amount of low-flash spirit being left in the semi-crude used by white spirit makers. This comes off at the commencement of distillation and is separated and passed over to the motor-sp refiners. Similarly at the end of the distillation a small tailin; high-boiling spirit is left in the stills which is useless as white s] and is turned over to the makers of burning and lubricating oil

Properties. The essential requirement for white spirit is tha must be completely volatile, but on the other hand must evaporate with extreme rapidity. It must therefore be free fr the highly volatile spirits previously described and also from non-volatile paraffins used as burning oils. As the volatility is all practical purposes proportional to the boiling point this requ ment is usually met by defining it as a petroleum distillate boil between 150° and 210°.

The following is an example of the range given by a sample good quality :

Under 150°	.	.	.	.	none
150 - 160°	.	.	.	.	18 per cent.
160 - 170°	.	.	.	.	35 ,,
170 - 180°	.	.	.	.	21·6 ,,
180 - 190°	.	.	.	.	12 ,,
190 - 200°	.	.	.	.	7·7 ,,
200 - 210°	.	.	.	.	5·7 ,,
Over 210°	.	.	.	.	none

These figures can only be taken as an individual example, actual figures varying with almost every sample.

It has already been made clear that petroleum is a materia complex and variable composition : white spirit, even that made fr oil from the same source, will vary accordingly from time to tim

its proportion of different hydrocarbons, and therefore in the relative proportion of the fractions distilling at different points. Taking into consideration the variations in the oil used by different makers and the varying efficiency of different distillation plants, it is obvious that absolute uniformity of distillation range cannot be expected.

The detailed distillation range of any sample is only of importance to the user as indicating its value for a particular purpose, but the limits to which all white spirits should conform are :—

The initial boiling point should not be below 140°.
The end point should not be above 230°.

The *flash point* is closely proportional to the boiling range and ranges from 75° to 100° F. The essential point is that it must be above 73° F. (23° C.) in order to comply with the regulations as regards inflammability for transport and shipping.

Within these limits the requirements of consumers as regards the volatility and flash point will vary somewhat in different industries and at different times. For example, a preparation made with white spirit intended for export to a hot climate such as India will stand a less volatile spirit with advantage than a preparation intended for consumption in this country. A spirit which gives the required rate of evaporation in this country will volatilise too quickly in a hot climate, and adjusting the preparation to the requirements of the market by using a higher boiling spirit has the added advantage that the flash point is raised automatically and the risk of danger in transport lessened. On this account it is usual for producers of white spirit to collect their distillate in fractions in separate tanks which can then be blended to produce a spirit to any detailed specification required. Most distilleries offer three or four standard grades of white spirit, to suit the requirements of different consumers. The following are the standard grades of one of the leading producers :—

Grade.	Specific gravity.	Boiling range.	Flash point.
Special (extra light)	0·784	143—180° C.	75° F.
No. 1 (light)	0·787	145—200	80
No. 2 (medium)	0·790	158—200	90
No. 3 (heavy)	0·794	160—210	100—105
No. 4 (extra heavy).........	0·807	180—220	125

The three standard grades suggested by Sauvage [4] are :—

	Light.	Middle.	Heavy.
Specific gravity	0·760	0·777	0·785
Flash point	86° F.	95° F.	104° F.
Distillation range	90 92% at 180°	90 92% at 200°	90 92% at 225°

For use as a paint and varnish thinner, a medium grade is requir The initial boiling point should not be below 150° : a lower boil point indicates the presence of hydrocarbons which evaporate rapidly and cause the paint to have a tendency to commence sett before it is properly brushed out. On the other hand, the (point must not be above 210°, as a higher limit implies a " tail ' non-volatile hydrocarbons which retard the drying and tend cause a weak film. The bulk, at least 90 per cent., should di between the limits 160° and 200°, and it is of real advanta if the fractions come over evenly between these two limits. I such purposes as metal polishes a lighter grade is desirable, as ra evaporation is required, whilst the heavier grades are preferable wax polishes. The slower evaporation reduces the tendency harden in the package on keeping and a *slight* residue on evaporat is an advantage rather than otherwise as it increases the elastic of the film of wax. This is only an advantage within limits, howev an excessive content should be avoided as causing the polish to over-elastic and have a tendency to smear.

The *specific gravity* of white spirit approximates to 0·8, l different samples vary within the limits 0·760 to 0·810. In samp derived from oil from the same source the specific gravity approximately proportional to the boiling range, rising with 1 increasing complexity of molecule of the hydrocarbons contain Thus No. 1 spirit has a lower specific gravity than No. 2, and so (As, however, the crude oil from different oil-fields varies considera in gravity, we find that identical fractions of spirit distilled fr oil of different origin will vary in specific gravity. This variatio due mainly to the relative proportions of the different series hydrocarbons present, as the unsaturated hydrocarbons of 1 olefine series, for example, contain a lower proportion of hydrog to carbon than the paraffin series and therefore a lower speci gravity for the same complexity of molecule. As the degree unsaturation is most marked with the aromatic series one finds general that a high content of aromatic hydrocarbons is acco

panied by a relatively high specific gravity for the same distillation range. Broadly speaking, therefore, the higher the specific gravity is in comparison to the boiling point the greater the value of the spirit as a solvent.

The following determinations of specific gravities of white spirit from different sources having exactly the same boiling range is due to Eugène Sauvage [4] :—

American	.	.	.	.	. 0·765
Persian .	.	.	.	.	. 0·772
Roumanian	.	.	.	.	. 0·776
Russian .	.	.	.	.	. 0·782
Borneo .	.	.	.	.	. 0·795

The *evaporation rate* of white spirit is of considerable practical importance. The evaporation of any volatile solvent is a function of the pressure exerted by the vapour coming off from it at ordinary atmospheric temperature. This is by no means directly proportional to the boiling point and varies greatly with different substances of the same boiling point.

In a substance like white spirit, which varies in boiling point owing to the varying proportions of the constituents of a mixture of substances of closely similar composition, the distillation range is an approximate guide to its evaporation rate. In such a mixture of hydrocarbons the lower boiling and more volatile hydrocarbons exert a higher vapour pressure than the heavier members, and when the liquid is exposed to the air in a thin film the vapour coming off contains a mixture in which the former predominates, leaving behind the higher boiling constituents which exert a lower vapour pressure and therefore evaporate more slowly. For most purposes it is of importance, not only that the spirit shall evaporate entirely in a reasonable time at ordinary temperatures, but that it shall evaporate at an even rate.

Illingworth has published [5] the results of careful experiments on the evaporation of white spirit in relation to its boiling range, from which it is abundantly clear that for paint manufacture 90 per cent. should distil below 200° and all at 218°. His paper contains an instructive series of graphs showing the volatility and vapour pressures of spirits of different boiling range, from which it is clear that in a spirit showing any content boiling above 200° the evaporation is uniform up to this point and then exhibits a marked drop or " tail." By isolating this tail fraction he showed that by

itself it would not evaporate in three weeks, whereas the remain
portion evaporated completely within sixteen hours.

The effect of such a " tail " is not only to retard the drying of
paint, but to produce a soft, tacky film; for it must be remembe
that the position is complicated in practice by the fact, that, inst
of the evaporation of the spirit alone used in these experiments,
have it evaporating from a solution in oil, which oil is oxidising a
increasing in viscosity at the same time.   Under such condition
is well established that even in the case of a highly volatile solve
the last traces become enmeshed in the drying film and only esc
very slowly.   The tendency of the " tail " is therefore to rem
permanently in the film.   This effect is found to a still grea
extent in varnishes, and it is in this respect that the inferiority
white spirit to turpentine as a varnish thinner becomes appare
Although turpentine exhibits a similar " tail " on evaporation, t
is due to the fact that it partially polymerises and oxidises duri
evaporation and the residue left in the film continues this acti
and ultimately hardens in conformity with the oil itself, becomi
part of the film, whereas any residue from white spirit remains
more or less permanent source of weakness.

The absence of such a non-volatile residual is generally det
mined by the " spot test," which is carried out by placing five dr
on a dry filter-paper and allowing it to stand for half an hour
ordinary atmospheric temperature, when the spirit should co
pletely evaporate, leaving no trace of greasy mark on the pap
A more reliable method is to place one drop of the sample und
examination and one drop of a standard sample side by side on
clean sheet of plate glass, and note the relative time of evaporati
to dryness and the absence of any greasy residue.   H. A. Gardne
has drawn attention to the fact that some grades of white spi
leave on evaporation a certain amount of dark-coloured, resino
residue which are objectionable, particularly if the spirit is to
used as the thinner for white paints.   To determine the presen
and amount of such residue he evaporates 100 c.c. of the spi
over the water-bath in a weighed copper dish, from six to thir
hours being taken for complete evaporation.

As it consists essentially of fully saturated and cyclic hydr
carbons, white spirit is chemically very stable and does not act
an oxygen carrier in the manner characteristic of turpentine.   T
drying of paints and other preparations made with it is purely
matter of evaporation as far as the thinner is concerned and
does not affect the drying of the oil in any way.

The *solvent power* of white spirit may be described as moderate. It mixes freely with all mineral and vegetable oils and is therefore quite satisfactory as a paint thinner, but is an indifferent solvent for oxidised oils such as blown oils, stand oils and thickened tung oil. The solubility of these thickened oils depends on the extent to which they have been polymerised and the quality of the white spirit. Cases frequently occur, particularly with gold size made from wood oil and rosin, where the addition of white spirit will cause precipitation of the resin and polymerised oil on standing for some time. Similarly, a blown oil will often dissolve in white spirit, but separate out again on keeping for some days. The same thing happens characteristically with the metallic salts of fatty acids such as lead linoleate and cobalt linoleate. Liquid driers prepared by dissolving such metallo-organic compounds in white spirit are very liable to separate out on keeping, particularly if chilled, unless very carefully prepared. Linoxyn is practically insoluble in white spirit and a thoroughly hardened paint film is not affected by it.

Freshly prepared rosin is freely soluble in white spirit, but rosin which has matured for some time and suffered the chemical changes which take place on storage is only partially soluble, leaving a considerable amount of insoluble residue.[7] The soft resins such as Damar and Manilla are moderately soluble, but generally form cloudy solutions and have a tendency to partially drop out of solution on storage. Hard resins are practically insoluble, except after melting and combining with oil. Oil varnishes made in this way can be thinned with white spirit, but the solution formed is not so stable as that made with such solvents as turpentine.

Paraffin wax and also vegetable and animal waxes dissolve fairly well in white spirit, but its solvent power for rubber is very indifferent.

Mention has already been made of the fact that the solvent power of white spirit is a variable quantity and its efficiency in this respect depends to a large extent on the oil from which it is prepared and especially the proportion of aromatic hydrocarbons it contains. American petroleum is particularly unsuitable for its production on this account and the period just succeeding the war, when the Eastern oil-fields were not available and white spirit prepared from Pennsylvanian oil was largely used, will long be remembered. This coincided with a period when the scarcity of turpentine caused the price to rise to an unprecedented level, and paint and varnish-makers were tempted to use white spirit to a greater extent than ever. The effect of substituting turpentine by this unsuitable

spirit, in varnish-making particularly, caused endless trouble ɛ
difficulty. These troubles largely disappeared with the reopen
of the Roumanian wells, which had been completely destroɔ
during the war to prevent them from falling into the hands of
enemy when Roumania was invaded.

In view of this liability to variation, and the practical importa
of solvent power in the use of volatile spirit, it is somewhat rema
able that definite requirements on this point are rarely laid do
in specifications. A standard test for the comparison of wh
spirits in this respect is highly desirable, but a satisfactory metl
is difficult to devise. Many methods have been suggested, but tl
are mostly empirical and open to considerable criticism.

Probably the most useful indication is given by determin
the content of aromatics, according to the method standardised
the Institution of Petroleum Technologists.[8] Holley [9] suggests
following method :—

> Prepare a short oil varnish by running 100 lb. of Kaɯ
> with 7 gallons of linseed oil and thinning with 25 to 30 gall
> of a standard white spirit. Place 2 oz. of this varnish iɪ
> 6 oz. graduated measure and add carefully 2 oz. of the sp
> to be tested, pouring it slowly down the side of the vessel
> as not to mix with the varnish. The two layers are now miː
> by vigorous stirring. If the varnish is thinned complet
> without any separation further additions of the sample
> made in the same manner in quantities of half an ounce a
> time until a permanent separation is obtained.

It is claimed that if properly conducted this test will give accur
information as to the solvent power of the sample examined, ɪ
vided precautions are taken to maintain a constant temperatɪ
and a uniform procedure in adding the thinner. It is, however,
difficulty of regulating these points, which are largely dependent
personal factors, and particularly the difficulty of preparinɡ
standard varnish, which makes this test unreliable as a basis
comparison between different observers, although it may be
considerable use for comparisons of different samples by the sa
observer over a limited period of time.

H. A. Gardner [10] uses a somewhat similar test, in which
employs a solid varnish prepared by incorporating oil with fu
resin without the addition of any thinner. A weighed quantity
this is melted and thinned with an equal weight of thinner. Spɛ
mens prepared in this way from different samples of white sp

are placed in cylinders and examined after standing for one month. Gardner also suggests [11] the use of blown oil as a test for solvent power. His procedure is to place a weighed quantity—5 to 10 gr.— in a tall, narrow beaker and add an equal weight of the spirit. The two are then mixed with a glass rod and the readiness with which the mixture takes place is noted. Successive portions of spirit are then added in the same manner, noting carefully the appearance and readiness of mixing, until a permanent milkiness occurs on mixing. The quantity added before this effect occurs is a measure of the solvent power of the spirit. The addition of further spirit beyond this stage results in part or all of the oil separating out on standing a short time.

White spirit is insoluble in water, but mixes in all proportions with most other organic solvents. Methyl and ethyl alcohols are exceptions, but the addition of a higher alcohol—butyl or amyl— causes a mixture of white spirit and alcohol to become mutually soluble.

White spirit made from a suitable oil which has been efficiently refined prior to distillation should be practically free from sulphur compounds. An inferior or improperly refined product is, however, liable to contain small percentages of various organic sulphur compounds. The presence of these is extremely objectionable in white spirit, as they react with metallic compounds such as lead, cobalt or manganese salts used as driers in paints and varnishes, causing discoloration. Such discoloration is noticed, for instance, when a varnish is thinned with a white spirit containing sulphur.

The original standard test for sulphur in white spirit was as follows :—

> Place 25 gr. of dry white lead in a small porcelain dish and mix thoroughly with 50 c.c. of white spirit. Cover with a watch glass, place on a steam bath for 2 hours, remove and observe the colour after 18 hours. There should be no appreciable darkening of the white lead. This test must be performed in an atmosphere free from hydrogen sulphide.

H. A. Gardner has suggested the following test as an improvement on the above [12] :—

> *Copper Strip Test.*—Place a clean strip of mechanically polished pure sheet copper, about ½ inch wide and 3 inches long (1·3 × 7·5 cm.) in a glass test-tube about ¾ inch wide and 18 inches long (1·9 cm. × 46 cm.). Add sufficient of the sample to be tested to completely cover the strip and heat

rapidly to its boiling point for 30 minutes, and then exam
the copper strip for blackening. A slight tarnish shall
disregarded, but any marked blackening shall be cause
rejection.

Gardner states that this test will detect active sulphur in wh
spirit when present to the extent of only 0·04 per cent.[13] He co
siders that the darkening of varnishes made with white spirit
not invariably due to sulphur, but may in some cases be caused
decomposition of some of the hydrocarbons in the spirit with t
formation of colloidal carbon.

These are only empirical tests suitable for the rapid judging
the quality of a consignment of white spirit; for accurate estimat:
the more elaborate procedure has been devised of burning a weigl
quantity of spirit, absorbing the products of combustion by asp
ation through sodium carbonate, oxidising the sulphur compoun
to sulphates and estimating gravimetrically by precipitation
barium sulphate.[14]

The *odour* of white spirit is one of its most useful properties.
not properly prepared it may retain traces of olefines and sulpl
compounds and is then liable to have a persistent and unpleas:
smell, but if properly prepared it has a characteristic smell, 1
pungent and less unpleasant to work with for prolonged periods th
that of almost any other organic solvent. Its toxic effect is ve
slight, and although it has been claimed that cases have occurr
of sickness amongst painters using paints thinned with white sp
in confined spaces, the writer in the course of many years l
never come across a case of even temporary ill-health amon
workers constantly using white spirit. The general experience
that workers constantly exposed to the fumes experience a headac
for the first few weeks, but seem to acquire immunity after t
and do not suffer any permanent ill effects.

In the early days of its employment as a paint-thinner, the gr
difference of the odour of white spirit from that of turpentine creat
considerable prejudice against its use, but cases are not unkno
in recent years of householders having rejected paint made w
American turpentine in favour of that made with white spirit
account of the comparatively penetrating smell of the form
The smell of an imperfectly refined white spirit can be improv
considerably by shaking it for some time with a small quantity
bleaching powder.

White spirit should be perfectly colourless and should eas

pass the test for water white (see p. 141). It should also be perfectly clear and free from any trace of suspended matter. At one time methods of refining were adopted by some distilleries which resulted in the spirit containing solid matter in colloidal suspension. Such brands appeared perfectly clear, but deposited a fine sludge on standing for a considerable time. The writer has come across samples during the past three or four years which formed such a deposit on standing in glass bottles for some months, but such products are now rarely met with and white spirit usually retains its crystal clearness and gives no deposit on standing indefinitely.

It is anhydrous, and is only capable of dissolving the slightest trace of water, and perfectly neutral in reaction. Any alkaline or acid reaction indicates a product of very inferior quality.

The principal use of white spirit is as a volatile solvent or thinner in paints, boot polishes, metal polishes, and floor and furniture polishes. For this purpose it has taken a recognised place and is used extensively and in large quantities. For the purpose of a thinner, where uniform and complete evaporation on exposure to the air is the essential requirement, it is perfectly satisfactory and has the advantage over such solvents as turpentine of low cost and the comparatively mild odour already referred to. Where other considerations have to be taken into account, however, the case is different. The relative value of white spirit as compared with turpentine as a thinner for high-class varnishes and enamels is a subject of frequent controversy, but in the present writer's opinion white spirit is essentially a thinner for paints rather than varnishes. Its solvent power for oils is practically equivalent to that of turpentine, but its solvent power for resins is distinctly inferior. In varnishes also its chemical inertness is a disadvantage. It lacks the oxygen-carrying properties of unsaturated hydrocarbons such as turpentine and tetralin, which facilitate the hardening of the film and exercise a certain bleaching effect on the oil.

Another purpose for which white spirit is extensively used is as cleaning agent in paint, printing ink and similar factories and for cleaning off oil from machinery, etc. It is preferable to either petrol or paraffin for such purposes, because petrol evaporates too rapidly and gives off a dangerously inflammable vapour, whilst paraffin does not dry off completely and leaves an objectionable residual odour. It is also preferable to turpentine for washing out painters' brushes, etc., as it evaporates without the oxidation and consequent resinification characteristic of turpentine, which tends to leave the brush slightly sticky and promotes the condition known

to the painter as " lousy." For such cleaning purposes, it is was
to use a paint-maker's grade of white spirit. The heavier grad
with an end point up to 230°, which are cheaper to produce, a
actually more efficient for the purpose, as the less volatile constituer
remain on the article cleaned for some time after evaporation of t
bulk as an extremely slight film sufficient to retard the rusting
metal containers, etc., and to keep the hairs of brushes in a flexil
condition.

Specifications for White Spirit.—The specifications for Aircr
Material issued by the British Engineering Standards Associati
include one for white spirit intended for use as a paint thinn
This has been widely used as the basis of contracts up to the prese
time. It contains the following technical provisions, together wi
sampling and inspection clauses :—

> *Reference.*—X. 20, dated July 1921 (see Chapter IX).
> *Description.*—Wholly a petroleum product, water-whit
> clear, free from water, visible impurities and objectional
> odour.
> *Specific Gravity.*—Not exceeding 0·800 at 15·5° C.
> *Flash Point.*—Not less than 75° F.
> *Distillation Range.*—Not less than 80 per cent. below 190°
>   Not less than 90 ,,   ,,   ,,   200°
> *Freedom from Grease.*—Determined by spot test.
> *Residue on Evaporation.*—Not to exceed 0·2 per cent.
> *Reaction.*—Neutral.
> *Freedom from SH_2.*—Determined by shaking 50 c.c. in a clo
> stoppered vessel with a small quantity of lead acetate soluti
> The lead acetate solution must not become coloured.

Similar specifications have been framed by the War Offic
Admiralty and other large consumers, to cover their requiremen

The recently formed Paint and Varnish Committee of tl
B.E.S.A. has been engaged in revising and consolidating the
specifications with a view to establishing one standard specificati
to cover the requirements of all consumers of white spirit for u
in paint and varnish manufacture. This new specification w
probably be issued shortly and will supersede the above.

The specification generally adopted in the United States, th
of the Bureau of Standards [15] (see p. 140), contains the followi
requirements :—

1. *Appearance.*—Shall be clear and free from suspended matter and water.

2. *Colour.*—Shall be " water-white."

3. *Spot Test.*—Shall evaporate completely from filter-paper.

4. *Flash Point.*—Shall be not lower than 30° C. (86° F.) when tested in a closed cup-tester.

5. *Sulphur.*—Shall be absent, as determined by the white-lead test.

6. *Distillation Range.*—Distillate below 130° C. (266° F.) shall not exceed 5 per cent. Distillate below 230° C. (446° F.) shall be not less than 97 per cent.

7. *Reaction.*—Shall be neutral.

The original specification contains detailed instructions for the laboratory examination for determination of these constants together with instructions for sampling and calculation of quantities.

Turpentine Substitutes.

White spirit was originally introduced as a cheap substitute for turpentine. It is still often referred to by this name and many firms offer turpentine substitute, generally under proprietary names suggestive of turpentine, which are nothing more than white spirit. In the present writer's opinion, this is a mistaken policy. An attempt has been made in the preceding pages to establish the fact that white spirit has a decided place of its own as a solvent and it should be supplied frankly on its merits. The word substitute in general implies inferiority. For some purposes white spirit is decidedly inferior to turpentine, for other purposes they are practically equivalent, whilst there are purposes for which it is actually superior to turpentine, and it would be sheer waste of money not to use it in preference. White spirit should not therefore be regarded as a substitute for turpentine, but as an entirely distinct solvent.

By blending two or more solvents one can, however, produce a close approximation to turpentine in its principal physical properties and such a combination can properly be called a turpentine substitute. Several preparations of this kind are offered under various proprietary names.

An effective turpentine substitute can be prepared, for example, by mixing a powerful solvent such as tetralin with white spirit and adding a small proportion of pine-needle oil to similate the odour of turpentine. The function of the tetralin in such a mixture is to increase the solvent power of the white spirit to that of turpentine

and to impart oxygen-carrying power. As the gravity, boi
point and flash point are considerably higher than those of turpen
a rather light fraction white spirit is used for the mixture and
adjusting the proportion between the two a mixture can be obta
which has the same flash point, evaporation rate and boiling p
as turpentine and is equivalent to it in solvent power. A sc
tifically prepared substitute of this kind is quite satisfact
Unfortunately, a great many so-called substitutes have been off
which are merely cheap imitations of the genuine article, q
different from it in properties.

Shale Naphtha.

The extraction of oil from bituminous shale has been pract
for a considerable time. The most extensively worked deposits
these of the South of Scotland, where the production of shale o
an established industry, but similar deposits are found in m
parts of the world. Extensive areas of oil-bearing shale are fo
in Estonia, north of Poland, for example. The working of t
for oil was started during the war and the production has devel
to considerable dimensions during the past five years.[16]

When such bituminous shales are subjected to destructive
tillation a greenish brown, viscous and evil smelling liquid is obtai
similar to crude petroleum. Originally this distillation was ca
out by charging the crude shale as mined into retorts simila
those used for the distillation of wood. In the most modern pl
the shale is subjected to a preliminary treatment, being ground
powder which is mixed with a substance, such as magne
chloride, capable of giving off hydrochloric acid, and pressed
briquettes. These are built up into the retort so as to allow
passage for the vapours liberated on heating, a more efficient
being obtained in this way. The function of the chloride is to c
a preliminary refining of the product by removing some of
undesirable by-products of distillation. The crude oil thus obta
is refined in a similar manner to petroleum, being first sepa
into two or three fractions by distillation. These are then w
alternately with sulphuric acid and alkali and fractionated.[17]

The more volatile distillates obtained are known as Shale Nap
or Shale Spirit. This is closely similar to petroleum spirit i
properties, but is inferior to it in quality for most purposes,
contains a higher proportion of the olefine series of hydrocar
It consists usually of 40 to 50 per cent. of olefines, the rema
being principally heptane, without any trace of aromatic h

carbons. The specific gravity is 0·718 to 0·730 and the distillation range 65° to 100°.

Shale naphtha is a water-white, very limpid liquid with a slight odour. It is insoluble in water and alcohol, but mixes freely with ether, turpentine, benzole, etc.; it readily dissolves all oils (except castor oil), some of the resins (such as gum damar) in the natural state, and nearly all when they have been partially decomposed by fusion. It is very volatile, and, unlike either turpentine or rosin spirit, evaporates without leaving any residue behind.

Shale naphtha is used to a certain extent as a motor spirit and for many purposes as an alternative to benzine. It is employed largely in Scotland as a solvent for rubber, as an alternative to coal-tar naphtha.

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CHAPTER II

COAL-TAR HYDROCARBONS

WHEN the tar obtained as a by-product in the destructive distillation of coal in gas works is distilled, the distillate is usually collected in from three to five fractions as the temperature rises, the method varying in different works. A usual classification is as follows :—

Light oils	80°—170°
Middle or carbolic oils	170°—230°
Creosote	230°—270°
Anthracene or green oils . . .	over 270°

Coal-tar Naphtha.

The " light oils " or " crude naphtha " is a dark brown, evil-smelling liquid, somewhat fluorescent in character, with a specific gravity of about 0·9. It is an extremely complex product containing both aromatic and fatty hydrocarbons, naphthalenes, and a wide range of derivatives such as phenols, pyridines, aniline, toluidine, thiophenes and other sulphur compounds.

In the crude state, coal-tar naphtha is used as a solvent for pitches in the manufacture of bitumastic preparations. The crude naphtha is refined by first purifying it by washing alternately with sulphuric acid and soda lye in a similar manner to petroleum. The treatment with sulphuric acid removes the unsaturated fatty hydrocarbons and some of the higher benzene hydrocarbons as well as thiophenes, whilst the caustic soda eliminates phenolic and similar compounds. The purification is completed by thoroughly washing with water.

All the coal-tar solvents, including benzol and solvent naphtha, and other industrial products such as the naphtha used as a fuel, are obtained from this refined naphtha by fractional distillation. The chief products thus obtained from the original tar are [1] :—

90 per cent. benzol . .	1·71 gallons per ton of tar	
90—160 solvent naphtha .	2·06 ,, ,, ,,
Heavy naphtha . . .	0·45 ,, ,, ,,
Carbolic oil	4·03 ,, ,, ,,
Creosote oils . . .	53·47 ,, ,, ,,
Pitch	13·55 cwt. ,, ,,

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Benzol.

On fractionating the refined coal-tar naphtha just described, the first portion to come over, below 130°, contains all the lower hydrocarbons of the benzene series and consists chiefly of benzene and toluene in variable proportions, with small quantities of higher homologues. This is generally known industrially as Benzol or Benzole.

The production of benzol from coal-tar naphtha is carried out in plant similar to that described under White Spirit. This statement should really be reversed to represent the facts correctly, for the production of benzols, etc., from coal tar was developed first and the refining of petroleum was originally modelled on gas-works practice and follows it in the main principles, with such modifications as experience of the difference between the two classes of product has shown to be desirable.

A further source of benzol was developed during the war, when the need for benzene, and especially toluene, became acute. Ordinary coal gas used as an illuminant contains a material proportion of benzol which is not really necessary for modern methods of illumination by incandescence. This benzole is therefore removed by the process known as " stripping." This consists of passing the gas through a washer or scrubber in which it is subjected to oil in the form of a fine spray. The oil dissolves out all the benzol and the resulting mixture of oil and benzole is then distilled to recover the benzol, the oil being used over and over again.

" Gas oil," a fairly heavy petroleum distillate, intermediate between paraffin oil and lubricating oil, is sometimes used for this operation. For the most part, however, a heavy creosote oil obtained from the coal tar is employed, having a distillation range of 210° to 300°. The important point is that there shall be a wide margin between the boiling point of the benzol and that of the oil so as to facilitate the separation by distillation. The crude benzol obtained is purified in the same manner as that obtained from the tar.

Benzol is a clear, colourless liquid with a peculiar and rather objectionable smell due to the presence of small quantities of impurities such as carbon bisulphide.

The approximate composition is :—

Benzene	.	.	.	.	60—75 per cent.
Toluene	.	.	.	.	24 ,,
Light hydrocarbons	.	.	.		4—6 ,,
Carbon bisulphide	.	.	.		2 ,,

The specific gravity varies considerably, from 0·865 to 0·900, according to the source of the tar from which it is distilled.   English benzols range from 0·880 to 0·888, Scotch average 0·870 and American from 0·879 to 0·882.   A higher gravity usually indicates an excessive proportion of carbon bisulphide.

Benzole sometimes contains pyridine to the extent of 0·1 per cent., which can be eliminated by agitation with sulphuric acid. Carbon bisulphide may be eliminated by converting it into potassium xanthate by treatment with alcoholic potash.

The removal of this impurity results in a marked decrease in the specific gravity and improvement in the smell if present in any quantity.   According to Nickels [2] :—

1% of CS_2 raises the specific gravity by 0·0033
2% ,,   ,,   ,,   ,,   0·0065
3% ,,   ,,   ,,   ,,   0·0093

Benzol is used as a solvent for oil-soluble dyes in the preparation of stains for woodwork, owing to its high penetrative power.   It is also used as an ingredient and diluent of paint removers and is added in small proportion to turpentine substitutes to increase their solvent power.

Its use as a solvent is, however, only incidental.   Its principal uses are :—

Motor Spirit.—It is used either alone or as an addition to petrol to improve the calorific value.

Artificial Dyes.—It is the raw material for the production of nitrobenzene, which on conversion into aniline forms the starting point of the aniline series of dyes.   It is also the starting point for synthetic indigo, etc.

Drugs.—It forms the raw material for many synthetic drugs.

Explosives.

For use as a solvent and extracting agent, benzol is further purified by refractionation and separated into several grades, usually denoted by the percentage distilling below 100°.

The highest grade is 100 per cent., which is a mixture of practically pure benzene and toluene.

The benzol used by the Air Board for the manufacture of aeroplane dope [3] must conform to the following data as regards physical properties :—

Specific Gravity at 15°.—0·883 to 0·886.

Distillation Range.—95 per cent. between 75° and 85°.

Residue on Evaporation.—Not more than 0·01 per cent.

Carbon Bisulphide Content.—Not more than 0·01 per cent. (the method of determination is prescribed in detail).

Free Acid.—Absent.

Colouration with Sulphuric Acid.—Not deeper than a 4 per cent. solution of $N/10$-iodine in distilled water.

Absence of Paraffin Hydrocarbons.—Must be completely sulphonated on treatment with sulphuric acid. (The method of determination is prescribed in detail.)

The ordinary industrial variety of benzol is 90 per cent. (*i.e.*, 90 per cent. by volume distils under 100°). A good sample should approximate to the following distillation range :—

80°—85°	25 per cent.
85°—90°	65 ,, ,,
90°—120°	10 ,, ,,
Over 120°	nil.

Fifty per cent. benzol should have the following range :—

Below 100°	50 per cent.
Below 120°	90 ,, ,,
Over 130°	nil.

This has a specific gravity of 0·867 to 0·880; it contains a larger percentage of xylenes than the 90 per cent. and generally a trace of carbon bisulphide.

The lowest grade is 30 per cent., which distils 30 per cent. below 100° and 90 per cent. below 130°. This contains only a small percentage of benzene, the bulk being toluene and xylenes.

Solvent Naphtha.

This is obtained as the next fraction in the distillation of refined coal-tar naphtha after the removal of the benzol. It owes its pronounced solvent power, combined with great volatility, to the presence of a large proportion of xylenes and cumenes, but has an exceedingly complex and variable composition, including, in addition to the above, a proportion of paraffin hydrocarbons and a small content of naphthalene.

Originally it comprised the whole of the distillate after removal

of the benzol or motor spirit and was extremely rich in xylenes, but much of this is now refractionated to supply the demand for pure xylene.   In addition to residual benzene, toluene and xylenes it contains cumenes and other aromatic hydrocarbons, small quantities of paraffins and olefines and traces of naphthalene and phenolic bodies.

It is a water-white liquid with a peculiar and rather unpleasant penetrating odour.   Some solvent naphthas have a tendency to lose their water-white condition on keeping and gradually develop a straw tinge, ultimately passing into brown.   This is particularly the case with those prepared from a crude naphtha obtained from producer gas tar.

Solvent naphtha is highly inflammable, burning rapidly with a very smoky flame.   It is miscible with alcohol, ether, turpentine, white spirit and nearly all organic solvents, and is a very powerful solvent for oils, fats, waxes, resins and india-rubber.   Solvent naphtha reacts readily with nitric acid, the aromatic hydro-carbons being converted into the nitro-derivatives, but is inert to hydrochloric and sulphuric acids, and is not acted upon by alkalies.

Two grades are generally recognised.

1. *Light Solvent Naphtha*, which distils 90 per cent. below 160°.   This has a flash point of 70–73° F. and a specific gravity of 0·865 to 0·875.   This grade is mainly used as a solvent for rubber, for which it is almost the only solvent of industrial importance.   For use in the rubber industry it is important that the initial boiling point should not be below 80°, indicat-ing that all the benzene has been removed, the solvent con-sisting of about 20 per cent. toluene and 80 per cent. xylenes. The absence of any material proportion of benzene is essential because of its highly toxic action, as the processes involved in the preparation of rubber necessitate the constant exposure of the workmen to the fumes of the solvent.   Before the dangerous toxicity of benzene was recognised several fatalities occurred in rubber factories owing to solvents containing it being employed.
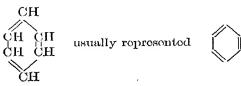
The value of solvent naphtha as a solvent for rubber lies in the fact that it causes the rubber to swell rapidly and thus considerably facilitates the working.   This grade is used to a smaller extent in many other industries, and their require-ments as to the proportion of benzene, toluene and xylenes

admissible vary somewhat and are usually met by specifying a definite distillation range.

The points that influence the selection of a particular fraction are :—

1. Toxicity.—If the process in which the solvent is employed does not involve exposure of workmen to the fumes, a proportion of benzene is admissible.

2. Flash Point.—If a flash point above 73° F. is essential a high fraction must be chosen.

3. Loss by evaporation is reduced by using a high fraction.

4. Greater freedom from residual solvent in finished goods is obtained by using a low fraction.

2. *Heavy Solvent Naphtha,* distilling between 160° and 190°, and usually specified 90 per cent. below 190°. This has a flash point of 95° to 100° F. and a specific gravity of 0·880 to 0·910. It is mainly used as a solvent and thinner for quick-drying paints such as anti-fouling compositions, and as a solvent for pitches. It is also used in conjunction with white spirit as a thinner for priming paints for woodwork. Its value in this direction is partly due to the fact that it has a greater penetrative power for wood than other solvents, and it is particularly useful for the priming of sappy or resinous woods. In addition to this, it has considerable toxic and germicidal properties. It therefore tends to preserve the wood by sterilising it and destroying any mould spores or insect eggs it may contain which facilitate its decay. It is also used as a thinner for cellulose varnishes and lacquers.

Benzene.

This is the fundamental compound of the aromatic or ring series of hydrocarbons. It has the empirical formula C_6H_6, and the structural formula generally accepted is that suggested by Kekulé, the carbon atoms being arranged in a closed chain, thus :—

usually represented

It is therefore an unsaturated body with 6 valencies latent and available for the formation of additive compounds.

The term benzene is by common consent restricted to the pure hydrocarbon, the coal-tar distillate already described, from which it is chiefly obtained, being known as benzol for distinction.

To prepare pure benzene, commercial benzol is agitated successively with dilute sulphuric acid, water, and milk of lime or caustic soda solution. It is then digested at 100° with a small quantity of concentrated sulphuric acid for several hours. This decomposes the sulphur compounds such as thiophene and the unsaturated hydrocarbons, olefines and acetylenes, which separate out as a black sludge. Fresh quantities of acid are added from time to time until no further discoloration of the acid takes place, indicating that these compounds are all removed.

The purified product is then subjected to fractional distillation. The portion distilling below 90° is collected separately and the benzene separated from its homologues by freezing, when it crystallises out at 5·5°, the higher compounds remaining liquid and being separated by vacuum filtration. To remove the last traces and obtain the benzene perfectly pure, this process of crystallisation is repeated one or more times.

Benzene is a colourless, very limpid liquid, with a high refractive index, 1·501, and a characteristic unobjectionable odour. It solidifies at 5·5° and boils at 80·5°. It gives off a highly inflammable vapour at ordinary temperatures, the flash point being 8°.

It is practically insoluble in water, but soluble in all proportions in the lower and higher alcohols and most other solvents. The specific gravity is 0·884 at 15°. It is readily identified by the smell, specific gravity, flash point and boiling point.

Benzene is now manufactured in large quantities of such purity that from 95 to 98 per cent. will distil within 1° of the theoretical boiling point. This is known as *crystallisable benzene*.

The purity of benzene may be determined by the following tests :—

1. Freedom from unsaturated hydrocarbons. 100 c.c. of the sample, when agitated with 20 c.c. of concentrated H_2SO_4 in a stoppered bottle, should show only a very slight coloration, not exceeding a pale straw yellow, after standing for several hours.

2. 10 c.c. are placed in a stoppered bottle and a saturated solution of bromine in distilled water is added drop by drop,

shaking after each addition until a yellow coloration is obtained which persists for at least 5 minutes. Not more than 0·5 c.c. should be required.

Toluene and Toluol.

Toluene, or methyl-benzene, is the next homologue in the benzene series of hydrocarbons, and consists of benzene with one hydrogen replaced by methane, thus :—

It is produced in the dry distillation of many resins, notably Balsam of Tolu, and is present to a considerable extent in coal-tar distillates. It is very similar to benzene in its technical properties, but a rather more powerful solvent. It is a water-white, readily volatile and inflammable liquid with an odour of the same general character as benzene, although there is a distinct difference, so that the two are quite readily distinguished when in a pure state.

It has a much lower solidifying point, below − 95°, and the boiling point, following the usual rule that the boiling point rises with the complexity of the hydrocarbon, is 111°. The flash point is 7°, the specific gravity is 0·881 at 0° and 0·871 at 15°. It has a refractive index of 1·496.

An almost pure toluene is obtainable commercially with a nearly constant boiling point ranging round 110°. Less pure commercial toluene is generally known as " toluol " for distinction, and is manufactured on a large scale. The boiling point of this should range between 110° and 120°.

Toluene forms the chief constituent of 50 per cent. benzol and is also present to a large extent in 90 per cent. benzol. It is employed for many industrial purposes, but is not extensively used as a solvent in the paint industry. On account of its great solvent power for waxes it is used as the solvent in the preparation of encaustic solutions for the preservation of stone and mural paintings.

Xylene and Xylol.

This is the third member of the benzene series and is benzene in which two atoms of hydrogen have been replaced by methane.

According to the position in which these are attached to the benzene molecule three varieties of xylene are formed, thus :—

Ortho-xylene.   Meta-xylene.   Para-xylene.

These vary in their chemical and physical properties, but in general they differ from benzene and toluene in having a higher boiling point and a lower specific gravity, and being more chemically active. Commercial xylene, generally known as xylol for distinction, is manufactured in considerable quantities by the fractional distillation of coal-tar naphtha. It contains the three isomeric xylenes in varying proportions, together with higher homologues, as well as hydrocarbons of other aromatic series and also paraffins. The ingredient of commercial value is meta-xylene, the other two isomers having a tendency to oxidise to form tarry matters.

Like benzene and toluene, xylene is a water-white, limpid liquid, with a boiling point of 139° and flash point of 21°. Commercial xylol has a distillation range of 135°—140° and a specific gravity of 0·865. The flash point is 30°. It is used to a considerable extent as a solvent for asphaltum and also in the printing industries for certain processes where a very even evaporation is essential.

Cyclohexane.

This is the hexa-hydride of benzene, produced by saturating it with hydrogen by passing a mixture of benzene vapour and hydrogen through a red-hot tube containing freshly-reduced nickel. Any unchanged benzene is then removed by treatment with strong sulphuric acid, which sulphonates the benzene but does not react with the hydride, which is a fully saturated hydrocarbon having the constitution

It is a liquid at ordinary temperatures, but solidifies at + 6°. The boiling point is 81° and the specific gravity 0·79. It has a refractive index of 1·426 to 1·429.

Cyclohexane has been prepared on an experimental scale, but it is not at present available in industrial quantities.

Tetralin.

This is a synthetic product, prepared by the action of hydrogen on naphthalene, the complex aromatic hydrocarbon obtained from coal tar. Naphthalene is a condensed benzenoid substance, containing 5 double bonds, and, theoretically, the hydrogenation of naphthalene can take place in five stages according to the number of double bonds in the molecule which are saturated. All these five possible derivatives have been prepared experimentally, namely, the di-, tetra-, hexa-, octa- and deca-hydronaphthalenes. Only two of these compounds are produced industrially; namely, the tetra-hydride, known as tetralin for short, and the deca-hydride, or dekalin, which is described in the next section; in these one and both of the benzene rings are saturated respectively, thus :—

Naphthalene, $C_{10}H_8$. Tetrahydronaphthalene, $C_{10}H_{12}$, or Tetralin. Decahydronaphthalene, $C_{10}H_{18}$, or Dekalin.

They are more readily produced than the intermediate compounds as the hydrogenation tends to take place mainly in these two stages, one or both of the benzene rings being saturated.

Thus Leroux [4] found that by hydrogenating naphthalene at 190° or higher temperatures he obtained pure dekalin, whereas at lower temperatures he obtained pure tetralin.

Similarly, one finds that if tetralin is treated with more hydrogen without carrying the reaction to completeness an intermediate product is obtained, known as *tetralin extra*. This is not, as one might expect, a mixture of all the intermediate compounds, but consists of tetralin and dekalin only. On fractionation, the mixture separates quite sharply into the two constituents.

The hydrogenation of naphthalene results in an alteration of physical properties as shown by the following data :—

	Boiling point.	Flash point.	Sp. gr.	Refractive index.
Naphthalene (solid) ...	218° C.	—	1·145	—
Tetralin (liquid)	205° C.	172° F.	0·980	1·5402
Tetralin extra (liquid) .	190—205° C.	140° F.	0·900	1·4815
Dekalin (liquid)	190° C.	135° F.	0·890	1·4672

It will be seen from this that there is a progressive change in properties, the naphthalene changing from a crystalline solid to a liquid, the boiling point being lowered by progressive hydrogenation, together with the specific gravity. There is also a distinct change in the odour on hydrogenation. The strong characteristic odour of naphthalene is apparent in tetralin, but considerably reduced, whilst dekalin has a characteristic smell of its own.

The production of tetralin was developed in Germany during the war in order to provide a substitute to fill the shortage of turpentine and petroleum distillates, and it was used both as a solvent and a motor spirit. It is now produced on a very large scale from naphthalene, which is a comparatively cheap by-product of the coal-gas industry.

Although the operation of hydrogenation is quite simple in theory, all that is necessary being to treat the substance with hydrogen in the presence of a catalyst, it requires considerable skill and experience to carry out the operation efficiently on a commercial scale. The process requires three essential ingredients for its operation :—

1. The raw material to be treated.
2. Hydrogen in a high state of purity.
3. A catalytic agent to induce the reaction.

The choice of a catalyst is a very important matter. A large number of substances are available and are used for various special purposes. Of these the most effective are finely-divided nickel and copper oxide. The former probably acts by forming an unstable nickel hydride which reacts with the unsaturated body, releasing the nickel for further action. Great care is needed in the preparation of the catalyst as the material is required in a state of absolute purity. The merest trace of some impurities will serve to poison the catalyst or prevent its efficient action. The purity of the hydrogen used is also of importance to the success of the operation. The slightest trace of an impurity, such as carbon monoxide or sulphur dioxide, for example, will suffice to poison the catalyst and lower the efficiency of the plant if it does not entirely prevent the reaction.

The usual method of preparing the hydrogen for the hydrogenation of naphthalene is by the purification of water gas. For this purpose the CO is removed from the water gas by treatment with superheated steam, when the reaction occurs :—

$$CO + H_2O = CO_2 + H_2.$$

The carbon dioxide is removed quantitatively by scrubbing with water under pressure, leaving the hydrogen perfectly pure.

The crude water gas, produced in large generators, must undergo repeated purifications to yield the chemically pure hydrogen necessary. For the same reasons, the raw materials used must be treated to remove any possible impurities, both chemical and mechanical, in order to ensure successful treatment. In the case of naphthalene, the greatest difficulty is to eliminate sulphur, which is always present in commercial naphthalene in the form of thionaphthene. This is found even in " pure " samples to the extent of about 0·25 per cent., which is quite sufficient to impair the efficiency of the catalyst.

The reaction between the three materials is carried out at a temperature of 150° under pressure in an autoclave fitted with efficient stirring devices to ensure ample contact between the hydrogen and the reagent. Unlike the hydrogenation of oils, where it is necessary to discharge the autoclave completely on completion of the reaction and separate the catalyst from the finished product by filtration, the hydronaphthalenes can be distilled off from the autoclave, leaving the catalyst behind and the autoclave can be charged and discharged in this way some fifty times without opening it. The reaction proceeds automatically and the end point can be readily detected by observing the increase of temperature and diminution of pressure which occurs.

Commercial tetralin attains a high degree of purity and has therefore a nearly constant boiling point. A sample examined by the author [5] gave the following results on a first fractionation :—

Up to 100°	.	.	.	2 c.c. (mainly water)
100°—205°	.	.	.	nil
205°—208°	.	.	.	182 c.c.
208°—210°	.	.	.	8 c.c.
over 210°	.	.	.	8 c.c.
				200 c.c.

Being only partially saturated, tetralin is capable of reaction in many ways. Its constitution may be regarded as ortho-xylol with the two aliphatic groups linked together by the group CH_2—CH_2, thus :—

Ortho-xylol.   Tetralin

Vollmann has shown that this constitution is confirmed by its chemical reactions. In general, tetralin behaves like a benzene derivative, although it is chemically more active. An exception to this is the fact that an alkaline solution of tetralin discolours potassium permanganate.[6]

Treated with concentrated sulphuric acid and then neutralised with alkali, tetralin yields tetralin–soda–sulphite, a white, soapy substance which is soluble in water and has a powerful emulsifying action. One can also form derivatives such as phenols and amines from tetralin. Thus tetrahydronaphthol or "tetralol" is manu-factured for use as a disinfecting soap, and various other com-pounds, such as tetrahydronaphthylamine, have been prepared in the laboratory.[7]

If tetralin (not recently distilled) is shaken up to an emulsion with water and starch, and potassium iodide solution added the well-known blue coloration appears. This reaction can be used for the detection of tetralin in benzols.[8]

Tetralin is also capable of autoxidation in the same way as other unsaturated hydrocarbons such as turpentine. A sticky film develops on the neck of a bottle in which it is kept for any length of time, the liquid gradually acquiring a pale straw colour. A similar reaction occurs if it is evaporated over a water-bath at a low temperature, when it turns yellow and ultimately resinifies. By evaporating 250 c.c. at a temperature of 80°, the author obtained a residue of 7 c.c. of a brown resin.

J. A. F. Wilkinson has pointed out that tetralin which has been stored for any length of time becomes miscible with alcohol in all proportions, whereas the freshly-prepared compound is not. This is ascribed to the development of oxidation products, which affect the properties of the liquid, in particular lowering the inter-facial tension between the tetralin and the alcohol to the extent of producing complete miscibility.[9]

Tetralin reacts to form coloured resinous substances with organic compounds of metals, notably the linoleate and resinate of man-ganese. This is rather a disadvantage to its use in thinners for white paints containing metallic driers, which are liable to develop a pink coloration owing to this reaction.

Lauffs has shown [10] that such discoloration of white paints by reaction of the tetralin only takes place in presence of manganese compounds, and if the use of manganese in the drier is avoided no difficulty is experienced in this respect. He suggests that tetralin may be used as a reagent for detecting manganese in white pig-

ments : if a sample is moistened with tetralin and dried on the steam-bath the presence of a minute trace of manganese causes a pink coloration. He claims that 0·005 per cent. of manganese in lithopone can be detected in this way.

The smell of tetralin is somewhat pungent and not so agreeable as that of turpentine, for instance, but the vapour does not produce any unpleasant effects.

Experiments on this point published in a report by the Ministry of Health in Berlin in 1920 indicate that it is without any toxic properties and the experience of the author fully confirms this. Although non-poisonous to human beings, it is, like naphthalene, destructive to insect life [11] and can be employed as a harmless insecticide for the preservation of fruit trees, etc.

Tetralin is not soluble in water and only slightly soluble in alcohol. But it is miscible with butyl and amyl alcohols and the addition of 10 per cent. of higher alcohol or benzol to a mixture of equal parts of tetralin and ethyl alcohol is sufficient to render them completely miscible.

Tetralin ranks as one of the most powerful solvents for oils and resins. It not only dissolves all vegetable oils but has a decided solvent action on linoxyn and for that reason is too powerful to use by itself as a paint thinner, as paint made with it would be liable to soften the undercoats. It does not act like alcohols in its solvent action and does not dissolve shellac and similar substances which are soluble in methylated spirit.

It has been stated [12] that tetralin is a solvent for synthetic resins of the phenol-formaldehyde type, but this has not been confirmed by the author, whose experience is that such resins are quite insoluble in tetralin— a partially polymerised resin of this type can be dissolved in a mixture of tetralin and butyl alcohol, but the tetralin will be found to separate out on standing.

The albertol type of synthetic resins are, however, soluble in tetralin, and the same applies to the synthetic resins prepared from coumarone, for which it is a good solvent. It is a strong solvent for waxes and rubber, but does not readily dissolve cellulose nitrate or acetate.

The rate of evaporation is considerably slower than that of turpentine. Vollmann [13] determined the respective rates by comparing the time taken for complete evaporation of an equal number of drops of equal size of different solvents on filter-paper. His

results are given as follows, taking the mean of three experim
in each case :—

	Sp. Gr.			
Tetralin	0·987	{4 drops in	93	minutes.
		{8 ,,	124	,,
Tetralin extra . .	0·904	{4 ,,	49	,,
		{8 ,,	69	,,
Turpentine . .	0·867	{4 ,,	15	,,
		{8 ,,	22	,,

Calculating the mean ratio between the results, one obtains
following relative ratio of evaporation :—

Tetralin .	.	.	.	.	.	6
Tetralin extra	.	.	.	.		3·2
Turpentine	.	.	.	.		1

Coleman and Bilham [14] found the relative rates of evapora
to be :—

				Ratio.
Tetralin extra .	.	. 0·0546 gr. in 91 minutes	2·890
Turpentine	.	. 0·0711 ,, 39 ,,	1

Schrauth and Hueter [15] give the percentage evaporation
different solvents per minute as :—

Tetralin .	.	.	. 0·14	Rosin Spirit .	.	.	
Tetralin extra	.	. 0·46	White Spirit .	.	.	
Russian turpentine .	. 0·48	Benzene	.	.	.	
Turpentine	.	.	. 0·58	Solvent Naphtha	.	.	

But although the rate of evaporation of tetralin is thus c
paratively slow, evaporation is very complete. Whilst it p
merises to a considerable extent if evaporated at a temperatur
80°, this only takes place to a very slight degree at ordin
temperatures.

Coleman and Bilham [14] give the percentage residue on evap
tion for tetralin extra and turpentine as 0·001935 and 0·01
respectively, or in the ratio 1 to 7·8.

The slow evaporation of tetralin combined with its str
solvent action renders it very useful in the preparation of p
removers. By using a mixture of tetralin and acetone one obta
a very powerful solvent, because the acetone attacks the fi
which is then held in solution by the tetralin and kept soft fo

sufficient time to enable it to be worked upon. At the same time it evaporates completely in a few hours, leaving a perfectly dry and clean surface for repainting.

The slow but complete evaporation combined with the great solvent power is also an advantage in the preparation of wax polishes and the like.

Reference has already been made (page 31) to the fact that by the combination of tetralin with white spirit a solvent practically equivalent to turpentine in its properties can be obtained, and a mixture of these two solvents forms a very satisfactory thinner for paints and varnishes. It can also be used with advantage, in combination with solvent naphtha, to slow down the evaporation and raise the flash point without impairing the solvent power.

Tetralin is a solvent for a large range of dyes and this, combined with its great penetrating power for wood, renders it a useful solvent for the preparation of stains for woodwork.

Dekalin

If tetralin is re-treated with hydrogen in presence of a catalyst under higher temperature and pressure than those required for its formation from naphthalene, it is converted into the fully saturated deca-hydride, the name of which is contracted for convenience in general use to Dekalin.

The further hydrogenation is accompanied by a further change in properties, the boiling point falling to 190°, the specific gravity to 0·890, and the refractive index to 1·4672. The odour of naphthalene entirely disappears, dekalin possessing a peculiar characteristic smell of its own, quite different from that of tetralin, resembling that of damp straw.

Being a fully saturated body it is chemically more stable and does not react to the same extent as tetralin. It does not resinify on evaporation, for example, and may be kept for prolonged periods without showing any change of properties.* Its vapour appears to be quite without physiological effect either on animal or insect life. Its solvent power is considerably less pronounced than that of tetralin. According to the author's experience it is practically equivalent to turpentine in this respect; it mixes in all properties with fatty oils and dissolves waxes and soft gums like damar, mastic and manilla in equivalent proportions to turpentine. It

* The discoloration in presence of manganese characteristic of tetralin does not occur with dekalin.

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does not, however, dissolve hard gums like kauri and copal does it attack linoxyn.

It is practically insoluble in water and alcohol but mixes w other organic solvents. The rate of evaporation is rather quic than that of tetralin and as there is no oxidation during evaporat it leaves no trace of non-volatile residue.

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CHAPTER III

THE TURPENTINE GROUP

THE solvents in this group, of which American turpentine is the most important member, are mainly derived from the resinous exudations of various species of pine and other coniferæ.

They consist essentially of mixtures of various members of the large and important group of aromatic hydrocarbons known as *terpenes*. These occur in nature as the principal constituents of the essential oils contained in a wide variety of plants, being present either free or in the form of derivatives—oxygenated compounds, alcohols or ketones. They are water-white liquids, with an aromatic smell, lighter than water and volatile without decomposition. The various members of the group are closely similar in their physical properties, the difference in composition between them being mainly in the grouping of atoms in the molecule. On this account the change from one member to another is very readily effected and many of them exist in two different modifications only distinguished by their action on polarised light; thus pinene exists as dextrorotatory and lævorotatory, the two varieties often occurring together in proportions which result in optical inactivity.

These characteristics render the isolation and classification of pure terpenes a matter of considerable difficulty. They are closely allied to cymene and camphor, all having the empirical formula $C_{10}H_{16}$ but varying considerably in constitution: they may be divided into three groups, of which the principal members are Pinene, Sylvestrene and Phellandrene respectively.

A considerable amount of work has been done on the constitution of the terpenes. Kekulé considered they were hydrocymenes, a benzene nucleus with a CH_3 and C_3H_7 substitution group in the para position. More recent investigations have, however, modified this view considerably. A full discussion of their constitution would be outside the scope of this work, but the following generally accepted formulæ for the pinenes are given as examples, as forming the most useful representation of the constitution indicated by their reactions :—

α-Pinene.   β-Pinene.

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For a complete account of the constitution of the terpenes refere should be made to a recent article by G. Dupont [1] and the works Vèzes and Dupont [2] and Heusler.[3]

The chief terpenes occurring in the various varieties of turpent are :—

	Sp. gr.	Boiling point.	Refractive index.	Optical activity.	Chief source
α-Pinene (Dextro-pinene, or Australene) .	0·858—0·860	156—160°	1·4655	+21	American turpenti
β-Pinene (Lævo-pinene, or terebenthene)	0·858—0·860	156—160	1·4655	—40	French turpenti
Dipentene	0·845	178	1·4731	nil	Elemi
Sylvestrene	0·848	176	1·4757	+66	Russian turpenti

The resinous exudations from the different species of pine tr contain these and other terpenes in varying proportions in co bination with solid resins. The name *turpentine* was origina applied to such resinous exudations, which were collected a used as varnishes in their original state of semi-fluid sticky mass The products from different trees were generally distinguished by t district in which they were chiefly obtained, the principal being :-

American turpentine—from the pines of America.
Strasbourg turpentine—from the white fir.
Bordeaux turpentine—from the French pines.
Venice turpentine—from the larch.
Canada balsam—from the Canadian balsam pine.
Copaiba—from the *Copaifera* of South America.

In mediæval times a crude method of distillation was employ in which this raw resin from the trees was placed in pithoi (t large earthenware jars used for storage of oil, wine, etc.); the mou of each pithos was covered by a sheepskin with the fleece si inwards. This apparatus was heated over the fire, when the vapo distilling from the resin was condensed in the sheepskin and subs quently collected by wringing out the fleece, a solid resin bei left in the vessel.

From this primitive method, the separation of the crude sen liquid resin into a volatile liquid and a solid resin developed into recognised industry. The solid resin became generally known

" colophony " or " rosin " and the liquid portion was called " spirit of turpentine " or " oil of turpentine." This name is nowadays very generally contracted to " turpentine " and, popularly, contracted further to " turps." As the name " oleo-resin " forms a convenient descriptive term for the natural product, it is a convenient practice, and one which will be adopted in this work, to use the name turpentine as a generic term for the volatile spirit obtained by distillation of the oleo-resin from any species of pine.

The composition of turpentine, which forms the most important solvent used in the paint industries, varies according to the particular species of pine tree from which it is derived, both as regards the proportion of different terpenes and the minor ingredients which it contains. There are thus numerous varieties of turpentine, having the same general characteristics, but differing amongst themselves in their exact physical and chemical properties.

The pine forests of one country usually consist entirely of one or two species of pine which differ from those in another country. Consequently the different varieties of turpentine are usually known by the country of origin and it is convenient to follow this classification. The principal countries producing turpentine, with the sources of their supply, are :—

Country of origin.	Sources.	
United States	Longleaf pine	*Pinus palustris* (or *australis*)
	Loblolly pine	*Pinus tæda*
	Pitch pine	*Pinus rigida*
	Cuban or slash pine	*Pinus caribæa*
	Swamp pine	*Pinus cubensis*
	Shortleaf pine	*Pinus echinata*
	Western yellow pine	*Pinus ponderosa*
	Spruce pine	*Pinus glabra*
Canada	Douglas fir	*Pseudotsuga taxifolia*
Central America	Mexican pine	*Pinus ayacahuite*
France	Maritime pine	*Pinus maritima* (or *pinaster*)
Spain	Spanish pine	*Pinus maritima*
	Aleppo pine	*Pinus halepensis*
Greece	Aleppo pine	*Pinus halepensis*
Russia and Poland	Scotch fir	*Pinus sylvestris*
Alsace	Silver fir	*Pinus picea*
Germany	Scotch fir	*Pinus sylvestris*
Austria	Black pine	*Pinus laricio* (or *nigra*)
Hungary		*Pinus pumilio*
Italy	Stone pine	*Pinus pinea*
India	Chir pine	*Pinus longifolia*
	Blue pine	*Pinus excelsa*
	Khasia pine	*Pinus khasya*
Japan	Japanese black fir	*Pinus thunbergii*

It will be noticed that with the exception of India and Cana
the British Empire is entirely dependent on foreign sources for
very large quantities of turpentine consumed. Some time
the Scottish Forestry Board investigated the possibility of est
lishing the production of turpentine from the Scotch fir, but a
exhaustive experiments came to the conclusion that the supply
oleo-resin was too limited to render its production a commerc
proposition. This is a matter for considerable regret in view of
threatened shortage of American supplies. It is difficult to beli
that with proper organisation the many districts in this count
particularly Scotland and Wales, where natural pine forests occ
could not be developed in a similar manner to those in France, a
a profitable industry created in otherwise barren districts.

The method of cultivating the trees and collecting and gradi
the oleo-resins belongs to the subject of resins rather than solver
and will not be considered here. For information on this subj
the companion volume in this series (T. H. Barry and R. S. Morr
—" Resins, Natural and Synthetic ") should be consulted.

The production of turpentine will be considered here to sta
with the distillation of the crude resin. This division of the subje
is rendered more natural by the fact that in many cases the turpenti
is not distilled in the country of origin; large quantities of ole
resin are imported into this country for distillation, the produ
being sold as " English distilled turpentine."

During recent years large quantities of varieties of turpenti
have been produced which are not extracted from the oleo-res
as just described, but are obtained by distilling the wood of tl
tree. In America, the two are distinguished as " Gum Turpe
tine " and " Wood Turpentine " respectively. French authoritie
however, define turpentine as an essential oil extracted by stea
distillation, at a temperature below 180°, from the oleo-resin of tl
living pine,[1] and consider that the spirit extracted from the woo
is not a true turpentine and should be classed as " pine spirits."

The production of turpentine is an industry of considerabl
dimensions. The consumption increased rapidly towards the en
of the nineteenth century and reached a maximum just prior t
the war, when the world output of all grades approximated t
45 million gallons. There was a considerable reduction during th
war, but in 1924 it had increased again to 42½ million gallons, an
it is estimated that at the present rate of increase an output o
50 million gallons will be required to supply the demand in th
course of a few years.

Of this total, it is estimated that the United States supplies at least 65 per cent. The production there has reached the limit of the forests and the demand is steadily outstripping the failing supply, a fact which is causing American producers to investigate searchingly every means of conserving their supplies by scientific methods of increasing the economy of production, schemes for afforestation and the exploitation of additional sources of supply.

The remaining 35 per cent. of the supply is mainly filled from France. The following is a recent estimate of the relative production in the various countries, in barrels of 50 gallons :—

United States	.	.	650,000	Greece	.	.	.	15,000
France	.	.	130,000	India	.	.	.	2,500
Spain	.	.	50,000	Miscellaneous	.	.	15,000

American Turpentine

The chief source of this turpentine is the longleaf pine (*Pinus palustris*), which is the most prolific species in the American forests, but practically every species of pine tree growing in large uniform tracts has now been examined and the oleo-resin from it tested to ascertain its suitability as a source of turpentine.[4] The chief centres of turpentine production in the United States are the Southern States, following the belt of the forests of longleaf pine along the Atlantic and Gulf coasts from Virginia to Texas, notably Virginia and Carolina. In addition to this main area of production the huge reserves of pine forests in other parts of America are now being exploited. The principal outlying districts where the industry has been established are the Philippine Islands and Mexico.

The production of crude resin from the pine in the United States appears to have been started at the close of the sixteenth century, although no reliable records are available until about a hundred years later. According to these records [5] the raw resin gathered from the trees was distilled in a crude and very wasteful manner by heating in open pans until all the volatile contents had been driven off, the residue being used as " pitch " for caulking ships. The amount of turpentine lost by these wasteful methods, adopted in the days when the pine forests appeared to be inexhaustible, is incalculable.

As the industry developed, the open pans were replaced by enclosed iron retorts and subsequently by the copper still with worm

condenser now used, which was introduced early in the nineteent[
century.

This copper still or " kettle " has a capacity of from 400 t
1000 gallons, the average size being about 7 ft. in height by 5 ft
at its greatest diameter. The bottom is concave and the to]
hemi-spherical with a circular aperture about 20 inches in diamete
to which is fitted a removable hood or " goose-neck " for carryin;
the vapours to the condensing worm. This latter is made of coppe
tubing, tapering from 6 to 8 inches in diameter at the inlet con
nected to the goose-neck to 3 inches at the outlet. It is abou
140 ft. in length formed into a coil about 6 ft. in diameter by 7 ft
high. The coil is fitted into a large wooden vat fed with a strean
of cold water, the outlet of the worm being led through the side o
the vat near the bottom and connected to receptacles for collectin;
the distillate.

The kettle is filled to about three-quarters of its capacity witl
the crude resin and the firing started. Distillation commence:
when the mass reaches the temperature of boiling water. The
distillate coming over first consists of a mixture of turpentine anc
water, which is collected in an open vat, where the water is separ-
ated by gravity, the turpentine, which floats on the top, being rur
off from time to time into barrels.

When the water present in the crude resin has all been driver
off, a small continuous stream of water is introduced into the stil.
and the distillation continued until the yield falls below the economic
limit. The water is then cut off, the fire drawn, the residual rosin
run out and the still prepared for a further charge.

The efficiency of the distillation depends on maintaining a
proper balance between the heat supplied to the still and the amount
of steam generated in it, so that the mixed steam and turpentine is
carried over into the condenser at a uniform rate and the boiling
mass is maintained at a steady level. If this is not properly con-
trolled there is excessive increase of volume, resulting in the con-
tents of the still boiling over into the condenser with contamination
of the turpentine and loss and danger of fire. As the water naturally
present is eliminated the ebullition in the kettle gradually subsides
and the volume of distillate reduces. The water is turned on at
this stage and the firing is carefully controlled so as to maintain
the proper balance of heat to convert the water and turpentine
to vapour at a uniform rate.

The effect aimed at is to keep the mass in the still in a state
of steady ebullition so that the distillate runs in a steady stream

containing approximately equal proportions of water and turpentine. As the end-point is approached the proportion of turpentine falls off and the temperature is raised so as to sweep out the last traces before drawing the fire and discharging the still.

The quality of the turpentine produced depends a great deal on the proper proportion of steam being distilled over with it to prevent the temperature inside the still rising too high with consequent partial decomposition and colouring of the distillate. This depends entirely on the judgment of the stillman, who as a rule works by rule of thumb, gaining his knowledge by experience handed down from father to son and being quite ignorant of technical principles.

The production of turpentine, in fact, is closely analogous to that of varnish-making, which was regarded until recently as a profound secret mainly because it depended on the accumulation of similar non-technical practical experience. In recent years, to continue the same analogy, these empirical methods have given way to more scientific control, based on investigation of the composition of the raw material and the reactions which take place on its distillation. Just as in varnish-making, the use of high-temperature thermometers has replaced the judgment of the still operator.

The first steps in this direction appear to have been made by Dr. Stephen Neal [5] who in 1906 experimented at his own distilleries in Georgia on the use of thermometers in the still to control the distillation. He devised a special form of thermometer for the purpose, similar to that now used by varnish-makers, and worked out the temperatures to be maintained at various stages of the operation. Since then scientific control has been steadily developed and a continuous and careful study made of the processes involved in the distillation, with great improvement, not only in the economy of production, but also in the quality of the product.

In the initial stages of the operation the temperature is maintained at 210° F.—the boiling point of a mixture of turpentine and water. As the natural water in the resin becomes exhausted this is indicated by a rapid rise of temperature to 315° F., the average initial boiling point of pure turpentine, technically known as the " water point." If this rise of temperature is left unchecked the turpentine would come over coloured and unsaleable.

When the temperature commences to rise in this way water is introduced and the stream so regulated that the temperature is allowed to fall until it reaches the " holding point " or temperature

which is known to be correct for the particular grade of resin being distilled. The temperature is kept steady at this point by regulation of the water and fire so long as the stream of distillate remains constant. When it begins to diminish, indicating the approach of the end-point, the temperature is allowed to rise again very slowly until it reaches 300° F. The water is then cut off, the thermometer allowed to rise a further five degrees and the operation is complete.

This method of distillation leaves nothing to guesswork and is absolutely certain to produce uniform results of the highest quality and quantity.

In order to obtain complete separation of the turpentine and water so as to avoid loss of turpentine, and the presence of water in the finished product, which is highly objectionable, an automatic separator is now utilised in the most progressive factories. This separator is adapted from that introduced in the French system and operates on the principle of utilising the difference in the specific gravities. It consists of a tank divided into several compartments. As the distillate from the condenser passes into the first compartment the water is discharged at a constant level and the turpentine overflows into the succeeding compartments, depositing in each any further traces of water that may be carried over, until in the last compartment it is quite clear and limpid and ready for storage.

The development of these scientific methods of production has become a matter of great importance at the present time in view of the imminent exhaustion of the supply of timber. If the old wasteful methods had been continued much longer the forests would have been exterminated by now.

American turpentine consists mainly of dextro-pinene. Its optical rotation varies from $+ 8$ to $+ 16$ in different samples whereas pure pinene has a rotation of $+ 21$. The difference is due to the fact that turpentine contains, mixed with the pinene, varying proportions of other inactive or lævorotatory terpenes, together with small quantities of derivatives.

According to Vavon [7] it contains :—

Dextro Pinene (australene) . . . 72 per cent.
Lævo Pinene (terebenthene) . . 28 ,,

Turpentine is a clear limpid liquid and when properly prepared should be perfectly colourless. Carelessness in preparation will result in a distinctly coloured product, which sometimes finds its

way into the market. Some samples are also liable to develop colour on exposure to sunlight.[8] In order to ensure uniformity in respect of colour definite standards have been agreed upon and specifications usually require the turpentine to pass the standard as " water white " (see Chapter IX).

American turpentine has a pungent odour that is quite characteristic and serves for its ready identification. It is quite distinct from that of other solvents, and whilst the whole turpentine group have a smell of the same general character, the individual products of different countries can be readily recognised by the variation in this property. This odour of turpentine is due to an aldehydic oxidation product which is present to the extent of about 1 per cent. This can be removed by treatment with sodium hydrogen sulphite solution, when the characteristic smell disappears, but soon returns on exposure of the turpentine to the air.[9] The smell of turpentine is not unpleasant in small quantity, but prolonged exposure to it is distinctly objectionable. Its effect varies very greatly with different persons, some being rapidly affected with headache and sickness, whereas others suffer no inconvenience at all. It is this physiological action of turpentine vapour which is largely responsible for the popular objection to the " smell of paint." It may be said in passing that whilst the unpleasant effects are by no means imaginary and extreme cases of susceptibility have been known to occur where definite illness has been caused by the vapour, the effect is in general merely temporary inconvenience during exposure. Painters constantly working with it soon acquire immunity and suffer no ill effects whatever from constant exposure to the vapour. The smell of turpentine was at one time regarded as the hallmark of a good paint, but with the recognition of the value of other thinners this is becoming less general. The author has even come across cases in recent years where paints thinned with turpentine have been definitely excluded on account of the pungency of the smell compared to that of alternative solvents.

Being a substance of complex composition, turpentine, in common with most other hydrocarbon solvents, has a variable boiling point. The recognised distillation range is from 150° to 180°. These limits are fairly constant and any marked variation indicates impurity. The regularity of the fractions coming over between this range vary somewhat in different samples, but not to the same extent as the petroleum distillates.

Turpentine is readily inflammable, burning with a smoky flame which deposits soot in large flakes, a peculiar odour being

evolved during the burning. The flash point averages 95° F (35° C.), varying from 90° to 98° F. in different samples.

When exposed to the air in a thin film turpentine evaporates almost completely, leaving no stain if tested by the usual method of pouring a few drops on to clean filter-paper and allowing it to stand for half an hour.

If the test be carried out under more critical conditions, however, it will be found that the evaporation is not absolutely complete, a slight trace of residue remaining. This is due to the fact that during the evaporation in presence of a large excess of air a chemical reaction takes place. From the outline of the chemistry of terpenes given above it is clear that they are unsaturated compounds and in presence of air they absorb oxygen with the formation of non-volatile resinous substances. The common experience that turpentine develops a sticky film on the neck of a bottle in which it is kept for any length of time is due to this action. This action is increased on warming and if turpentine is exposed to warmth and light under conditions in which it cannot evaporate rapidly it increases in viscosity to the consistency of honey (*see* Fat Turpentine, p. 65). If turpentine is evaporated under carefully controlled conditions it will be found that a definite residue is obtained. Coleman and Bilham,[10] by evaporating 17 gr. in a steam oven at 100°, obtained a residue of 0·1516 per cent. The amount will vary according to the length of time the turpentine has been stored.

Apart from this polymerisation, the evaporation of turpentine is perfectly regular and uniform. Illingworth[11] has described an experiment in which the evaporation was so conducted as to approach as nearly as possible to the conditions existing during the drying of a painted surface. He exposed 200 c.c. in a trough 75 cm. by 30 cm. in area so that the film was 0·9 mm. thick. This trough was kept level, and at intervals of an hour the spirit was poured off and its volume measured, the loss being obtained by subtraction from the initial volume. The time of draining the tray was always the same, and, in order to compensate for the trace of spirits still adhering to the tray, an addition was made to the reading of the residue, this addition being determined by the mean of several estimations of the loss experienced in at once pouring off 200 c.c. of spirit under the conditions used in the experiment. Another factor, determined upon the loss experienced in pouring off 100 c.c., was used when the residue was under 100 c.c.

The results of these experiments are given in the form of a graph in which the curve is practically a straight line, showing that on evaporation the turpentine " loses approximately the same amount per unit of time whether the interval be taken early or late in the experiment." The evaporation is therefore perfectly uniform and regular.

These evaporation properties of turpentine account for its great popularity and unique position as a thinner for paints, and more particularly for varnishes and enamels. The hardening of a varnish made with turpentine is perfectly uniform because the turpentine evaporates uniformly and at the same time acts in conformity with the drying oil, increasing in viscosity by absorption of oxygen. There is considerable evidence for thinking that under the conditions which obtain in the drying of paints and varnishes the turpentine acts as a carrier of oxygen to the oil, absorbing oxygen from the air and giving it off again in contact with the oil and thus facilitating the drying of the film. Any non-volatile residue formed during the evaporation becomes part of the film and acts in conformity with it, ultimately hardening to a solid resin by further polymerisation. This property of polymerising on drying is characteristic of the terpene group of solvents and is shared only by the partially saturated hydrides of naphthalene described above (p. 43).

The specific gravity of turpentine is fairly constant, ranging from 0·860 to 0·880, the average figure being 0·867. The variation is mainly due to the extent to which polymerisation has taken place, and a high figure generally indicates a turpentine that has been stored for some considerable time. For commercial purposes the gravity is usually calculated as $8\frac{1}{2}$ lb. to the gallon. The refractive index at 20° ranges from 1·466 to 1·478.

The solvent power of turpentine exactly answers to the requirements of a paint and varnish thinner. That is to say, it dissolves readily all vegetable and mineral oils, but does not dissolve the linoxyn formed by the drying of a paint film, so that a fresh coat of paint and varnish made with it can be put on a previous coat after drying without bringing it up. It dissolves soft resins such as rosin, damar and Manilla, but only dissolves the copals and similar hard resins after they have been " run " and subsequently combined with oil. As a solvent for mineral waxes it is not quite so good as the coal tar hydrocarbons, but it forms a good solvent for animal and vegetable waxes and a solution of beeswax in turpentine is largely used as a furniture polish. As a solvent

for rubber it is quite inadmissible, as its oxidising properties c
rapid perishing of the rubber.

Turpentine is practically insoluble in water, but water is so
in it to a slight extent and it generally contains traces. It i
soluble in glycerol, but mixes in all proportions with the m
hydric alcohols. A mixture of turpentine and methylated s
will tolerate the addition of a small percentage of water wit
separation. The mutual solubility of turpentine and alcohol
been worked out in detail by Vèzes and Moulin.[12] It mixe
all proportions with all other organic solvents.

Turpentine, being an unsaturated body, is chemically ac
If kept in an iron or steel container for any length of time
metal will corrode, particularly along the surface of the li
which develops a reddish colour due to colloidal oxide of i
This action can be prevented by protecting the inner surfac
the container with a lacquer of shellac or synthetic resin,
storage in iron tanks so protected has given satisfactory res
Zinc or galvanised-iron containers cannot be used unless prote
in the same way, as the exposed metal is attacked with forma
of zinc salts, which give a turbid appearance to the turpentine.
most common practice is to use either tinned iron or wooden ve
for storage. Owing to its acidity and oxidising action turpen
has a destructive effect on fabrics and its use in connection
artists' canvases, where extreme durability is essential, shoul
avoided.

This power of oxidising on exposure to air has already l
referred to in connection with its behaviour on evaporation.
exact reactions which take place are exceedingly complex
little understood. Similar reactions occur in turpentine on sto
for any length of time; the viscosity increases, the specific gra
and boiling point rise, whilst the optical activity decreases. So
times crystals of pinol hydrate ($C_{10}H_8O_2$) may settle out o
resinous deposit form consisting of polyterpenes. The acidity
increases on storage and the odour changes considerably, becom
less pleasant. These changes are principally due to the grad
conversion of the pinene, partly by oxidation and partly by c
version into dipentene, limonene and other secondary terpe
Kingzett and Woodcock [13] have shown that this oxidation
accompanied by production of material quantities of formic a
acetic acid and aldehydes.

By agitation with hydrogen in presence of platinum bl
turpentine can be hydrogenated to the saturated compound, $C_{10}H_{1}$

Turpentine reacts vigorously with nitric acid to form various oxidation products. With concentrated nitric acid the reaction is so vigorous as to cause spontaneous combustion.

Like other unsaturated compounds, it absorbs halogens readily; the reaction is also very vigorous and can take place with explosive violence.

The absorption of iodine is utilised as a test for the purity of turpentine in the same way as for oils. The *iodine value* recorded by different observers varies considerably, from 282 to 380. This variation is, however, largely due to differences in the method of determination rather than to actual differences in the turpentine, as has been shown by E. M. Taylor.[15] On treatment with bleaching powder in presence of water turpentine can be largely converted into chloroform.

Turpentine also reacts with sulphuric acid, polymerising to form terebene and colophene ($C_{20}H_{32}$). As most of the substances, such as petroleum, used as adulterants for turpentine, are not acted upon by sulphuric acid, this reaction forms a useful method of determining the purity of turpentine. This test was first elaborated by Candless[16] and has been adopted in most official specifications. The B.E.S.A. standard polymerisation test is :—

" Forty c.c. of concentrated sulphuric acid (1·84 sp. gr.) shall be placed in a suitable graduated vessel and the whole immersed in iced water. Ten c.c. of turpentine shall then be slowly added and gradually mixed with the acid, care being taken that the temperature does not rise above 60° C. (140° F.). When the mixture no longer warms up on shaking, the whole shall be thoroughly agitated and the vessel placed in a water-bath and heated to between 60° C. and 65° C. (140° F. to 149° F.) for 10 minutes, the contents being thoroughly mixed by shaking vigorously five or six times during this period. The vessel should be kept unstoppered during this operation.

The vessel shall then be cooled to room temperature and allowed to stand for 12 hours. The residue shall be washed, the amount determined and its refractive index taken."

Specifications for Turpentine.—In this country turpentine is in exactly the same position as regards specifications as white spirit. The existing B.E.S.A. specification (X. 21, dated July 1921) contains the following provisions :—

Description.—Of good colour, free from water and other visible impurities.

Residue on Evaporation.—Not more than 2 per cent. weight.

Specific Gravity.—0·860 to 0·880 at 15°.

Flash Point.—Not less than 90° F.

Distillation Range.—Initial boiling point 150° : not less th 90 per cent. below 175°.

Refractive Index.—1·468 to 1·478 at 20°.

Polymerisation Residue.—Not more than 6 per cent., witl refractive index not less than 1·500.

U.S. Bur. Stand. Specification [18] is framed to cover both " gun turpentine and wood turpentine. The requirements are :—

Appearance.—Shall be clear and free from suspended mat and water.

Colour.—Shall be " standard " or better (see Chapter IX).

Odour.—Shall be characteristic of the variety of turpent specified and, if desired, shall conform to the odour of the sam agreed upon.

	Maximum.	Minimum
Specific gravity, 15·5/15·5°	0·875	0·862
Refractive index at 20°	1·478	1·468
Residue after polymerisation with 38N-H_2SO_4 .		
Gum spirits—		
Volume (per cent.)	2·0	—
Refractive index at 20°	—	1·500
Wood turpentine—		
Volume (per cent.)	2·5	—
Refractive index at 20°	—	1·495
Initial boiling point at 760 mm. pressure.........	160° C.	150° C.
Distilling below 170° at 760 mm. pressure (per cent.)	—	90

The original specification contains detailed instructions for carry out these tests.

This specification is identical in all technical points with that the American Society for Testing Materials.[19] The Specification the United States Navy [20] is closely similar, the main difference be that a Flash Point not below 34° C. (93° F.) is specified in additi

As turpentine is produced in comparatively small quantit by a large number of firms in different districts, and the r material varies in composition from time to time, it is liable variations in quality which do not indicate adulteration, and the United States qualities which do not come up to the Stand Specification are recognised as low-grade pure turpentine.

The classification of grades proposed by Veitch and Denk [21] is

	Polymerisa-tion Residue per cent.	Sp. gr.	Refractive index.	Distillation range.
Standard	1	0·862—0·870	1·468—1·476	95% below 170°
No. 2	1	0·862—0·875	1·468—1·480	90% below 170°
No. 3	1	0·865—0·880	1·468—1·485	60% below 170°

Rectified Oil of Turpentine.—This is a purified turpentine, prepared by treating it with an alkali to saturate the free acids and redistilling with steam. Jobson [22] prepares this by agitation of the turpentine with a solution of sodium hypochlorite for 1 hour, followed by distillation with live steam.

Fat Turpentine.—If turpentine is kept at a temperature of about 80° or is exposed for a considerable period to air and sunlight it undergoes a gradual combined process of oxidation and polymerisation, ultimately changing into a liquid of syrupy consistency. This was used formerly by artists and is still employed to a small extent as a medium in pottery and glass painting and in certain photographic processes.

Oxidised Turpentine.—In the manufacture of synthetic camphor, pinene is extracted from turpentine, and the residue containing the other terpenes mixed with various chlorine derivatives is left as a by-product and used under this name. It resembles Pine Oil, but has a higher boiling point and slower evaporation.

Terebene is a mixture of dipentene and other hydrocarbons prepared by mixing turpentine with sulphuric acid and shaking. The treatment is repeated until the turpentine is optically inactive, and the product is then steam distilled.

It is a colourless liquid of characteristic odour, of the same general character as turpentine, slightly soluble in water. The boiling point should approximate to 160°, but ranges from 156° to 180°, and the specific gravity at 15° ranges from 0·862 to 0·866. When freshly prepared it is quite neutral, but on exposure to light and air it changes in a similar manner to turpentine, becoming acid, acquiring a yellow colour, and gradually resinifying, forming a sticky deposit on the neck of the bottle in which it is kept.

French Turpentine.

Turpentine is produced in France from the maritime pine (*Pinus maritima*), which is found mainly in the sandy regions

5

along the S.W. coast bordering the Gulf of Gascoyne, a dist
known as the Landes. The exploitation of these pine forest
of comparatively recent date—until about a hundred years
the region in which they now grow was a barren marshy tr
practically uninhabited. The pines were first planted with
object of holding back the sand from encroaching on the la
and it was not until 1857 that the drainage of the land resul
in the complete afforestation of this district.

It was only when the world's supply of turpentine and re
was withheld during the American Civil War that the possibili
of the Landes district as a source of turpentine were appreciated a
the necessary impetus was given to develop the present magnific
forests. Although it is therefore much more recent than
American industry, the French turpentine industry, having be
developed on scientific lines from the first, has reached a mu
higher state of efficiency.

The outstanding features of the industry are the systema
planting of the trees and the working of them in sections so th
the supply is continuous and there is no waste or destruction
the forest. The permanency of the supply is safeguarded by
systematic replanting of the forests in proportion as the trees
or are felled.

The resin is collected in a similarly systematic and economi
manner and brought to the works for distillation. There a
about 120 distilleries in the Landes district; their methods
operation vary somewhat, the principal processes employ
being :—

1. The primitive method, employed by the oldest wor
consists of simply heating the crude resin over an open f
in a manner similar to the early practice described und
American turpentine.

2. Steam distillation. The turpentine in this process
distilled off by means of high-pressure steam in a mann
similar to that practised in America.

3. Vacuum distillation. This is a modern modification
the steam distillation process, in which, in place of steam und
pressure, water is added to the resin and heated under reduc
pressure.

The turpentine is collected from the still into reservoirs a
distributed in tank wagons. The yield obtained from the ol
resin is :—

Turpentine	. . . . .	15—20 per cent.
Resin	. . . . .	65—75 ,,
Other products	. . .	5—10 ,,

The annual output of French turpentine, prior to the war, was about 20,000 tons. About 50 per cent. of this output was used in the country, the remainder being exported, chiefly to Germany, England, Switzerland and Austria.

The production in recent years is given by Vèzes and Dupont [23] as follows :—

1914 .	. 19,000 metric tons	1918	.	20,000 metric tons
1915 .	. 15,000 ,,	1919	.	25,000 ,,
1916 .	. 17,000 ,,	1920	.	36,000 ,,
1917 .	. 17,000 ,,			

The scarcity of turpentine, and consequent high prices ruling in recent years, has resulted in steadily increased output by intensive culture. At the present time the bulk of the product is used in France, the surplus available for export being about 17,000 tons. Most of this is absorbed on the Continent and very little French turpentine is used in this country. On this account only a brief summary of its technology has been given here, but it should be mentioned that the French turpentine industry has formed the subject of the most exhaustive technical study, which is embodied in the monumental works of Vèzes and Dupont,[24] which should be consulted for detailed information.

French turpentine is closely parallel to American in composition and properties, but differs in details. On account of the highly organised method of production it is more constant in its proportions and less liable to variation. Like American turpentine, its main constituents are lævo- and dextro-pinene, but the proportion is different, the lævo predominating.

According to Vavon [14] the proportions are :—

Lævo-pinene	. . . . .	63 per cent.
Dextro-pinene	. . .	37 ,,

On this account French is distinguished from American turpentine in rotating the plane of polarised light to the left, the amount varying from 18° to 40°.

The principal physical constants are :—

Boiling range .	.	.	.	.	155—170°
Specific gravity	.	.	.	.	0·857—0·872
Refractive index	.	.	.	.	1·468—1·478
Flash point .	.	.	.	.	86—90° F.

The odour of French turpentine is less pungent and more pleasan than that of American and sufficiently different in character t render it easy to differentiate between the two. In all othe properties and in its general chemical reactions French is identica with American turpentine, and as a solvent it is practicall equivalent.

Indian Turpentine.

Both turpentine and rosin have been produced in India on small scale for many years. The chief source of the oleo-resin i the Chir pine (*Pinus longifolia*). Smaller quantities are derive from the blue pine (*P. excelsa*) and the Khasia pine (*P. Khasya* The turpentine is extracted at two distilleries, one in the Punja and the other in the United Provinces. The amount produced i steadily increasing, but it does not yet cover the requiremen of the country. The developments possible are very consider able, as there are huge areas of Chir pine forests available fo exploitation.

According to a recent estimate the total areas occupied b resin-yielding pines are :—

Pinus longifolia	.	.	.	.	3,300 sq. miles
,, *Khasya*	.	.	.	.	1,800 ,,
,, *Merkusii*	.	.	.	.	1,200 ,,
,, *excelsa*	.	.	.	.	200 ,,
,, *Gerardiana*	.	.	.	.	100 ,,
	Total	.	.	.	6,600 sq. miles

Of this only about 200 sq. miles have been exploited up to th present, and it is estimated that the possible annual productio of turpentine is 2 million gallons.

The first investigations on the production of turpentine tool place about 1890 and operations were started in 1896,[25] the proces being based on the French system of production, which has beer

modified from time to time to suit local conditions. The output in 1903 was 125 tons, which has steadily risen to approximately 1,000 tons in 1922—23. The industry is entirely worked under Government control.

The chief difficulty experienced in expansion of the industry is that of transport of the raw material to the distillery, which in many cases has to be located some hundred miles or so from the source of supply and along very indifferent roads.

On arrival at the factory the oleo-resin is placed in a vat and melted by steam and allowed to stand, when the water, dirt and other impurities sink to the bottom and the clean oleo-resin is drawn off into storage tanks, from which the still is fed. In order to ensure the efficiency of this clarifying operation the melted resin is generally thinned with a little turpentine from a previous distillation. This lowers the viscosity and specific gravity and ensures a thorough settlement of the water and dirt. If this is not done the specific gravity of the melt approximates to that of water so closely that it is difficult to obtain a complete separation. The still in general use is a steam-jacketed cylinder which can be maintained at any desired temperature by regulating the pressure of the steam. The still having been charged with oleo-resin steam is injected into it and the turpentine and water vapour coming over pass through a trap still, to separate out any resin that may be blown over, into a condenser. The mixture of turpentine and water from the condenser is passed into a mechanical separator and the crude turpentine obtained is re-distilled and passed through lime water to remove any traces of abietic acids. The last traces of water are removed by tanking.

The average yield from the crude oleo-resin is :—

Turpentine	.	.	.	.	20 per cent.
Resin	.	.	.	.	70 ,,
Dirt and impurities .	.	.	.	3 ,,
Water	.	.	.	.	7 ,,

The composition of this turpentine differs from American, the principal constituent being a terpene hitherto unknown, which has been named Longifolene, related to sylvestrene, but differing from it in properties. According to the report published by the Imperial Institute this constituent is present to the extent of 60 per cent., the remainder being chiefly lævo-pinene. The later exhaustive work of J. L. Simonsen [26] has shown that lævo- and dextro-pinene

are the principal constituents and that there are two new terpene associated with them :—

d-Carene, boiling point . . .	168°—169°
Longifolene ,, . . .	254°—256°

The proportions in which these are present are, according to Gibson and Smythies :—

d-Pinene	60·8 per cent.
d-Carene	14·8 ,,
Longifolene	10·2 ,,
Residue and loss	14·2 ,,

The distillation range is from 165° to 175°. The following give the mean of five samples examined at the Imperial Institute :—

Up to 165°	1 per cent.
165°—170°	56 ,,
170°—175°	29 ,,
Over 175°	9 ,,
Residue	5 ,,

If the distillation is not carefully conducted the end-point is higher still, constituents from the resin coming over with a boiling point above 175°. Great care is therefore taken to ensure a slow and steady distillation and to stop it before these high-boiling fractions begin to come over. In order to ensure the complete removal of such fractions the turpentine is re-distilled and separated into three grades. The first grade is specified as 90 per cent. under 170°, specific gravity 0·865 and an evaporation residue under 1 per cent.

Indian turpentine has a rather slower evaporation rate than American and oxidises more rapidly. The relative residue left on slow evaporation in open dishes is :—

Indian	1·25
American	0·25

The solvent power, according to experiments carried out at the Imperial Institute,[25] is not so great as that of American turpentine. These data apply to the Chir pine turpentine, which is the principal product. That derived from the *Pinus excelsa* is superior in quality, having a lower boiling point (157°—160°) and a more pleasant

odour. It is, in fact, practically identical with the American article, consisting almost entirely of dextro-pinene.

Spanish Turpentine.

The production of turpentine in Spain amounts on an average to 6,000 tons per annum, of which about 4,000 tons are exported. The industry has been carried on in a very primitive manner as a peasant industry from a remote period. The first distillery appears to have been erected in 1848, but proved a failure owing to the difficulty of transport and the conservatism of the peasants,[27] and until 1862 the pine forests were practically untouched. In that year a distillery was started at the instigation of two French-men, Messrs. Falcon Bros.,[28] who introduced the system of collecting the gum in vogue in the Landes and later developed the steam system of distillation. Other factories soon followed and an industry was developed, but owing to French competition and ruinous price-cutting it was almost brought to a standstill in 1879. This resulted in a gradual consolidation of the whole industry, with the result that in 1898 it had become a practical monopoly of one syndicate with a capital approximating £1,000,000, controlling all the distilleries.

The pitch pine from which the turpentine is derived is not worked in one area as in France, but is scattered all over the country. The best forests are found in the centre of Spain near Madrid.

The resin, which is collected under the French system, is very rich in turpentine and the distillation is effected in a similar manner to the French, some working on the mixed system, some by steam distillation and some the vacuum process. The turpentine is well distilled and is practically equivalent to the French product.

Minor Sources of Turpentine.

Greek Turpentine.—This is obtained from the Aleppo pine (*Pinus halepensis*), the gum from which yields approximately 20 per cent. turps and 70 per cent. rosin. The turpentine in this country is also a by-product of the wine industry, the raw resin being dissolved in the wines of the country to form " resinato." Much of the turpentine is not distilled from the crude resin but from the wine dregs. It has the following physical data :—

Specific gravity	0·855—0·863
Optical activity	+ 38°—41°

Greek turpentine has a very pleasant vinous odour. The average output is 14,000 casks of 50 gallons, about 3,000 tons.

Portuguese Turpentine.—This is produced on the French system, the annual production being about 2,000 tons.

Algerian Turpentine.—Recently the production of turpentine has been commenced on an experimental scale by the French system. The principal tree here is the Aleppo pine, of which there are some 7 million acres. There is also a small industry under French control in Corsica, where the Corsican pine and the maritime pine grow to about an equal extent.

German Turpentine.—It is strange that the extensive pine woods of Germany do not appear to have been exploited for turpentine until the stoppage of outside supplies by the war forced attention to domestic supplies. The industry was started in 1916, modelled on the most advanced American methods, and had developed an annual output of 5,000 tons by 1918.[29]

Austrian Turpentine.—The centre of the industry is in Southern Austria, where extensive forests of the Black Pine (*Pinus laricio*) are found. The turpentine produced closely resembles the Spanish product; it is lævo-rotatory (36°—39°), with a specific gravity of 0·863—0·867 and a refractive index of 1·469. According to Dupont and Barraud [30] it has the composition :—

Pinene	.	.	.	.	.	96 per cent.
Limonene	.	.	.	.	1	,,
Sesquiterpenes	.	.	.	1	,,
Oxidation products	.	.	.	2	,,

Japanese Turpentine.—The Japanese black fir is utilised to a small extent to produce turpentine, but at present the industry is unorganised and the product poor in quality.

American Wood Turpentine.

This name is generally applied to the variety of turpentine obtained in America by extraction of the stumps of the pine trees left in the ground when the original forests were cleared for timber. When a pine tree falls down or is felled, and is allowed to lie on the ground and rot, the resinous portions of the wood are comparatively durable and remain intact for long periods of time after the less resinous portions, particularly the sapwood, have decayed and disappeared. Stumps left in the ground decay in the same manner, and it is these residuals of resinous wood—natural con-

centrates, as one may term them—which are collected under the name of " lightwood," " fat wood " and " pine knots " and utilised in the production of wood turpentine.

The first attempt to utilise this waste pine timber as a source of turpentine dates back to the middle of the nineteenth century. The first to carry out the distillation of the wood on a commercial basis appears to have been James Stanley, who erected a small plant in 1872 in North Carolina.[31]   His process was not, however, a great success, the product being more in the nature of creosote than turpentine; and it was not until about 1900 that wood turpentine began to attain industrial importance.[32]   It has only been by a process of trial and error, and by the gradual accumulation of experience at the cost of many expensive failures, that the production of a satisfactory article has been established on a commercially successful basis.

When these stumps were first utilised as a source of turpentine they were subjected to destructive distillation, which produced a very inferior turpentine of bad colour and smell and contaminated with methyl alcohol and acetic acid; a product, in fact, which was not really turpentine but more of the nature of tar spirit. Wood turpentine is still produced to some extent by this destructive distillation process.   The process is closely parallel to that of the distillation of hard woods in the production of wood spirit, etc. (see p. 88), the wood being loaded into retorts the design of which is a modification of those used in Europe.   In conducting the process it is important that the temperature of the retort should not rise above 200° until all the turpentine has been extracted from the wood, otherwise it becomes contaminated with other products from which it cannot be readily purified.   The distillate which comes from the condenser is a brown liquor of complex composition which is purified by re-distillation.

In addition to the wood turpentine, this destructive distillation process yields a number of other products—pine oil, tar oil, wood tar and in some cases wood alcohol, acetate of lime and creosote. The most modern retorts are constructed of re-inforced concrete fired internally, the heat from the fire being conveyed by means of cast-iron flues.   Perkin [33] describes an electrically heated retort which is used in Vancouver.

Wood turpentine prepared by destructive distillation cannot be obtained perfectly free from by-products, and therefore possesses properties different from other turpentines and should be classed with the tar spirits.

Although the advantage of distillation with steam to produ
a more satisfactory product had been recognised for many yea:
the practical difficulty encountered was that of obtaining a sat
factory yield, as it was difficult to secure penetration of the wo
by the steam in order to extract the turpentine. It was not un
this was overcome by the evolution of machinery for reduci:
the wood to the state of coarse powder that steam distillati
became a practical success. According to J. E. Lockwood [34] t
first steam distillation plant to operate successfully was put i
on the Mississippi in 1909. In this process, which is now rapid
superseding dry distillation, the wood, previously reduced to sm:
chips, is fed into an extractor and distilled with steam in a simil
manner to the oleo-resin.

This simple steam distillation process produces the best gra
of turpentine, but the yield is not economical. The most mode:
plants employ a modification of this process in which the powder
wood is first subjected to live steam in a digestor to extract t
turpentine and pine oil and then boiled with petroleum spirit
dissolve out the resin. This extraction is carried out in seri
each charge of wood after steaming being washed with sever
charges of solvent on the multiple extraction system. After t
extraction is completed the charge is finally steam distilled
recover the solvent.

The operation of the steam distillation process, although appa
ently simple, requires considerable skill and experience to produ
a uniformly satisfactory product. The more carefully it is co
ducted the more closely does the product approximate to th
obtained from the oleo-resin. Slow and regular distillation at
low temperature is essential in order to obtain the maximum conte
of original pinene. Rapid distillation results in the conversion
the terpenes with excessive formation of dipentene. The detai
of design and operation of the plant vary considerably in differe
works, and according to the process and the quality of wood use
the yield of turpentine varies from 4 to 8 gallons per ton
wood.

In the fifteen years or so that wood turpentine has been on th
market the production has steadily increased and it is estimate
that to-day it approximates to 10 per cent. of the total output
turpentine. As a general rule the wood turpentine distilleri
are more modern in design and equipment and work on a muc
larger scale than the oleo-resin distilleries, and are consequentl
able to produce a more standardised and uniform product.

It is claimed [34] that as the forests available for the production of oleo-resin become depleted the wood-distilled product will eventually become the predominant supply of American turpentine.

As now prepared by the steam distillation process wood turpentine is closely similar to ordinary American turpentine, the main difference between the two being that the wood turpentine contains a material proportion of dipentene and a proportion of limonene and terpinene. This gives it a smell quite distinct from that of ordinary turpentine, but has the advantage of increasing its solvent power.[35] Dipentene has double the number of unsaturated atoms in the molecule to pinene and therefore acts more vigorously as an oxygen carrier.

The physical data are as follows :—

Colour	Water white and perfectly clear
Specific gravity	0·860—0·863
Initial boiling point	150°—153°
Distillation range	90 per cent. below 170°
Flash point	34°—36°
Refractive index	1·4668—1·4694 at 20°
Polymerisation residue	3—4 per cent.
Iodine value	282—352

The following analysis of an individual sample is given by Sherwood [36] :—

Initial boiling point	151°
Percentage distilled below 170°	90·5
Residue on polymerisation	1 per cent.
Specific gravity at 15°	0·865
Flash point	34°
Refractive index	1·469

It will be seen that these constants differ from those of ordinary American turpentine. The difference is quite characteristic of wood turpentine, being mainly due to the partial replacement of pinene by the higher boiling dipentene. The high boiling point must be distinguished from that of a badly prepared " gum " turpentine containing high fractions of oxidised resin oils. Apart from this difference in physical properties and the slight difference in smell there is nothing to distinguish wood turpentine made by the steam distillation process from that distilled from the oleo-resin.

Pulp Turpentine.

A further variety of turpentine is obtained in America as by-product in the preparation of wood pulp by treatment wit alkalies. The pulp is boiled with a mixture of caustic soda, sodium sulphide, sodium carbonate and sodium sulphate. A vapour come over with the steam during the boiling which contains turpentin mixed with various other organic compounds. The turpentine ha a bad smell owing to the presence of mercaptans and other sulphu derivatives.

According to B. R. Armour [37] this turpentine can be free entirely from the mercaptans and other impurities and converte into a product equal in all respects to genuine American turpentine His process consists essentially in treating the crude turpentin with the hypochlorite of an alkaline earth in combination wit water " under non-acid conditions." By this means all the im purities are rendered inodorous or separated out so as to be readil removed by mechanical means.

French Wood Turpentine or Pine Spirit.

The development of the wood turpentine industry in Americ and the high price ruling for turpentine have encouraged investigatio on the possibility of supplementing the supply of French turpentin from the maritime pine by distillation of the wood as well a extraction from the oleo-resin. Investigations by Michel Jaffard [3] showed that the residue of resin left in the wood after collectior of the oleo-resin compared favourably with that of the longlea pine. The matter has been fully investigated in the laboratorie of the Institut du Pin by Dupont and Michaud.[39] As in America the main concentration of resin lies in the stumps of old tree which have been left in the ground to decay for some years.

By distillation of these stumps with steam, Dupont and Michau obtained a product which on fractionation yielded approximatel 30 per cent. of pine oil and 70 per cent. of a spirit which closel resembles French turpentine, but differs from it in a similar manne to the difference between American wood turpentine and " gum ' turpentine. In view of the difference in composition it is con sidered that this product cannot be regarded as equivalent t French turpentine, particularly for chemical and medical purposes and it is suggested that it should be distinguished by the name pine spirit (*esprit de pin*).

Russian Turpentine.

Russian turpentine (sometimes known as Polish, Swedish or Finnish turpentine) is obtained from the Scotch fir (*Pinus sylvestris*), immense forests of which are found in Russia, Poland, Finland and Scandinavia. The production is now practically at a standstill, although before the war the annual production was about 4,000 tons, most of which was exported in the crude state and refined in this country. The chief centres of production are Archangel, Poland, Lithuania and the Kazan district.

The industry appears to have been started about 50 years ago, mainly as the result of the initiative of an Englishman who formed a local company to organise the export of turpentine to England to take the place of American turpentine, which was scarce at that time. In 1873 it had developed to the extent of exporting 150 tons of crude resin. Just prior to the war strenuous efforts were being made to establish the industry on more efficient and economical lines.

Russian turpentine is produced entirely by destructive distillation of the wood and is characterised by an extremely pungent and penetrating odour, which produces unpleasant effects on the user. This odour is extremely difficult to get rid of, although Perkin [33] claims that properly refined Russian turpentine cannot be detected from American by the smell. It is a question, however, whether such efficient refining can be carried out as a commercial proposition on account of the cost of the process and the loss involved. The more rational plan of improving it would be to improve the method of production, as has been adopted in America, so as to avoid these undesirable by-products. A still better plan would be to develop the production of turpentine from the oleo-resin.

There is an unlimited supply of untouched pine forest awaiting exploitation, and there seems little doubt that once the country has developed a stable government the turpentine industry could be established in Russia to produce enormous quantities of turpentine equal in quality to American or French.

The composition of Russian turpentine is complex and variable. The principal constituent is the secondary terpene, Sylvestrene, which is present to the extent of about 70 per cent. Dextro-pinene forms from 10 to 15 per cent. and there is a similar proportion of cymol, the balance being small quantities of creosote and hydrocarbons of high boiling point.

Sylvestrene has a very high positive optical rotation. Russian

turpentine accordingly has a higher optical activity than any other turpentine, ranging up to $+$ 24.

Russian turpentine is rarely obtained water-white like true turpentine, but generally has a decided straw colour which deepens on storage, particularly if exposed to light. It evaporates rather more slowly than American wood turpentine and leaves a high percentage of residue. It absorbs oxygen more freely than true turpentine and rapidly increases in viscosity on standing. The physical properties are :—

Boiling range	160°—180°
Specific gravity	0·862—0·875
Flash point	95°—100° F.
Refractive index	1·476

Tar Spirit.

If the crude tar obtained by the destructive distillation of wood is re-distilled, a volatile spirit is obtained which is employed to some extent as a solvent. The principal source is Stockholm tar, and a similar product is obtained as a by-product in the production of wood turpentine by the destructive distillation process. When freshly prepared, tar spirit is a light straw colour, but it gradually darkens on exposure to light, ultimately turning to a dark brown and viscous liquid.

It has a mild but penetrating odour of creosote and is extremely complex in composition, containing terpenes, creosote, acetone and various phenolic bodies. The physical constants are very variable, but the boiling range usually runs from 160° to 270° and the specific gravity from 0·9 to 1·0.

It evaporates rather slowly and leaves a slight non-volatile residue, on account of which the odour persists for a long time. It is, in fact, closely allied to Russian turpentine, which is sometimes sold as tar spirit. In France these wood distillation products are classified thus :—

Fraction boiling below 150° . . .	Wood benzine
Fraction boiling between 150° and 180° .	Pine tar spirit
Fraction boiling above 180° . . .	Pine tar oil

On account of its content of ketones tar spirit has a strong solvent power and is useful for the preparation of black stoving varnishes, being a good solvent for pitches.

Pine Oil.

Pine oil is a by-product of the wood turpentine industry of comparatively recent introduction. It comes over with the distillate in the production of turpentine by the steam distillation of the pine wood and is separated from it by fractional distillation. According to a process patented by Teeple,[40] the product is purified subsequent to distillation by alternate treatment with alkali and hydrochloric acid followed by final washing with sodium carbonate solution.

Pine oil is also obtained as a by-product in the manufacture of wood pulp by the sulphite process (cf. p. 76). The crude distillate is refined by boiling with very dilute sulphuric acid and re-distilling with superheated steam at slightly reduced pressure.[41]

It is a light straw-coloured oil with a pleasant odour resembling that of pine-needle oil. The physical data are :—

	R. C. Palmer.[42]	Teeple.[43]
Specific gravity at 15°	0·932—0·935	0·935—0·947
Refractive index at 20°	1·4798—1·4815	1·4830
Boiling point ...	190°—195°	206°
Distillation range	90% between 190° and 218°	75% between 206° and 218°
Acidity	below 0·1 per cent.	—
Moisture content .	below 1·25 per cent.	3—4 per cent.
Flash point	76°	—
Optical rotation .	—	—11

The composition of pine oil is mainly secondary terpenes, probably derived from the original pinene in the wood. In addition to intermediate products such as dipentene it contains a large proportion of terpineol, and smaller quantities of borneol, cineol, camphene, and various phenolic bodies, together with some free fatty and resinous acids. It also contains ketonic and aldehydic substances, to which the odour is due.[44]

It is used as a slow-drying solvent in many directions, being an excellent solvent for gums and resins, and is useful for many purposes on account of the powerful and very agreeable smell it imparts. It has the exceptional property of being actively germicidal, although non-poisonous to human beings. On account of this lack of toxicity combined with its pronounced smell and unpleasant taste it has been suggested as a denaturant for alcohol.

Pine-needle Oils.

The needle-like leaves of practically all varieties of conifer
trees, particularly pines, yield an oil when distilled with stea
the amount and character varying with the particular class a
species of tree. The production of these oils has long been
established industry in many parts of the Continent. These c
are also prepared in many parts of Canada and the United Stat
but the industry is there unorganised and intermittent in charact

The " oil " thus obtained is really a volatile spirit analog
to turpentine in composition, consisting essentially of a mixture
several members of the terpene group, principally limone
sylvestrene, phellandrene and dipentene, the proportions of wh
vary in the oils obtained from different species of tree. They di
from turpentine in containing only a small proportion of pinene.

These oils have a strongly penetrating and pleasant odour
pines, which has been identified as due to bornyl acetate, wh
is present in varying quantities, from 5 per cent. to as much
30 per cent. in some varieties.

The physical constants of the various oils have formed t
subject of considerable research (the results of which are summaris
in Allen's " Commercial Organic Analysis," Vol. IV, p. 380).

These varieties of aromatic oils are produced in considera
quantities, but they are used mainly as deodorants for other solven
particularly the petroleum solvents, in the preparation of polisl
for boots and shoes, floors, furniture, etc. Their value in this c
nection lies in the fact that, in addition to their property of impa
ing an agreeable odour, they are similar in general properties to t
solvents to which they are added and do not impair their solv
power in any way. They are also largely used for spraying purpos
to impart a fragrant odour to hospitals and public rooms, and a
for medicinal purposes.

Terpineol.

This is derived from terpene hydrate by the action of dilu
sulphuric acid. The empirical formula is $C_{10}H_{17}\cdot OH$ and t
following structural formula indicates its chemical behaviour :—

$$(CH_3)_2 - C - OH$$
$$CH$$
$$CH_2 \quad CH_2$$
$$CH_2 \quad CH$$
$$C$$
$$CH_3$$

According to the relative positions of the methyl groups, three modifications are possible. The commercial preparation contains all three of these, the α-variety predominating.

According to Coffignier,[45] it is prepared commercially by the prolonged digestion of the following mixture :—

Turpentine	10 parts
Alcohol (90°)	15 ,,
Sulphuric acid (sp. gr. 1·640) . . .	5 ,,

It is also extracted from pine oil, which contains it in large proportion.[43]

As the boiling point of the pure α-modification is 219° and that of the β 210°, the commercial preparation varies between these limits according to the relative proportions present, the usual figure being 215°. Similarly, the specific gravity ranges from 0·923 to 0·940.

Terpineol is a liquid with a strong odour resembling lilac. It is a powerful solvent and capable of dissolving most of the hard resins in the cold. On this account its use was proposed by Tixier some years ago for the preparation of varnishes from hard resins without fusion. According to Tixier, Kauri, Pontianak and Manilla are totally soluble in terpineol, and the hard copals like Sierra Leone and Angola are largely soluble, giving very pale solutions.[46]

Tixier took out a patent for this process, but the varnish produced by it did not prove commercially attractive, and terpineol is not utilised to any great extent as a solvent at the present time. The price at which it can be produced as compared with other modern solvents rather handicaps its use, but its possible applications in connection with cellulose and other types of modern finishes deserves further investigation.

Hydroterpin.

This is a synthetic product, made by treating pine oil with hydrogen under pressure in presence of a catalyst in a manner similar to that described under tetralin. Zinc is found to be the most satisfactory catalyst.[47]

It is a water-white liquid, with a pleasant, mild, aromatic smell, having the following physical properties :—

Distillation range	179° to 195°
Flash point	47°
Specific gravity at 20° . . .	0·879
Bromine number	38
Refractive index	1·4733
Optical rotation	+ 4

6

The evaporation rate is practically identical with that of Ameri
turpentine.   It is claimed to be equivalent to American turpent
in solvent power and to form a satisfactory substitute, as it agr
with it in properties more closely than any other solvent available

Rosin Spirit.

When rosin is subjected to destructive distillation a dark bro
viscous oil is obtained having pronounced fluorescence, together w
an impure aqueous solution of acetic acid.

The production of rosin oils and rosin spirit in this way fr
the waste and low-grade rosins produced in the turpentine indust
is mainly due to the work of Frémy, who studied the possibili
in this direction early in the nineteenth century; most of the r
oils are prepared by the process he introduced, which cons
essentially of dry distillation of the rosin.   The crude distillat
treated with caustic soda to neutralise the free acid and re-distil
to produce the commercial rosin spirit.

This refined rosin spirit is an almost colourless liquid, somew
resembling turpentine but differing in physical properties.
smell is quite characteristic and quite different from that of
of the turpentines.   The specific gravity varies considerably, fr
0·856 to 0·883, but it is invariably heavier than American turpenti

On heating, rosin spirit distils with constant rise of temperatu
the boiling point ranging from 115° to 250°, the end points and
proportions coming over at different temperatures varying wid
with different samples.

The flash point ranges from 36° to 38° C. (97° to 102° F.).

This variable boiling point is an indication of the complex
of its composition, which includes a large range of decomposit
products of the original terpenes.   According to Renard [48] it c
tains pentane, pentene, toluene, hydrotoluene, and substances suc
cymene; about 50 per cent. consists of hydrocarbons with boil
points below 120°, notably heptine, C_7H_{12}.

Rosin spirit is insoluble in water and alcohol, but is soluble
ether, or a mixture of alcohol and ether, also in turpentine, chlo
form and white spirit.   Nitric acid acts on it rather less energetic
than on turpentine, forming a dark scarlet mixture; hydrochlo
acid has but little action.

When properly refined, and entirely free from the non-vola
rosin oil, rosin spirit forms a good solvent for oils, and it was larg
used at one time as a substitute for turpentine when the sup

was short, as it could be produced at a comparatively low price by the distillation of inferior grades of discoloured rosin. It does not form a really satisfactory thinner for paints, and is inferior to white spirit as an alternative to turpentine, as it evaporates in an irregular manner, leaving a viscous residue which dries badly and hinders the oxidation of the oil. With the advent of the abundant supplies of petroleum solvents and the introduction of the other modern solvents its use has considerably decreased and it is little used in the paint industry at the present time.

Oil of Spike.—This is a product of similar character to turpentine, obtained by distillation of spike lavender (*Lavandula spica*). It is sometimes known as lavender oil, but must be distinguished from the true lavender oil used as a perfume. It has a pleasant smell slightly reminiscent of lavender, but quite distinct from that of the perfume. The specific gravity is 0·85 to 0·88 and the boiling point 170° to 200°. It is used to a small extent as a solvent in the preparation of artists' mediums and ceramic colours. It was at one time largely used as a medium for stained-glass painting, but has been generally superseded by gum water for this purpose.

Gurjun Spirit.—Certain species of *Dipterocarpus* found in Indo-China yield an oleo-resin known as Gurjun balsam. By distilling this with steam in the same way as pine resin an essential oil can be extracted which is closely similar in properties to turpentine, only higher in specific gravity and boiling range. The collection of the crude balsam is at present unorganised and the supply uncertain, but the raw material appears to be abundant and to form a possible source for industrial development. According to J. Cuénot [49] trials of its use as a varnish solvent have given excellent results.

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CHAPTER IV

THE ALCOHOL GROUP

THE alcohols are a large and important group of organic compounds derived from hydrocarbons by the substitution of hydroxyl for one or more of the hydrogen atoms in the molecule.

They compare, very broadly speaking, with the alkalies and other inorganic hydroxides in their ability to combine with organic acids to form compounds, analogous to salts, known as esters. The well-known synthetic resin " ester gum," formed by the action of glycerol on rosin, is an example.

Ethyl alcohol is by far the most important of the alcohols from the practical point of view, so much so that it is a convenient and well-established practice for the term alcohol, when used without any qualification, to imply ethyl alcohol, other members of the group being always distinguished from it by giving the full name. Modern practice tends to carry this further and establish similar names for the higher and lower homologues of ethyl alcohol in industrial use. Thus :—

Methanol signifies Methyl Alcohol.
Alcohol ,, Ethyl Alcohol.
Propanol ,, Propyl Alcohol.
Butanol ,, Butyl Alcohol.

In the following pages the practice has been adopted of using the two names as synonymous and interchangeable.

Methanol or Methyl Alcohol.

This the simplest member of the alcohol series, being the methyl hydroxide derived from methane or marsh gas, CH_4, by the introduction of one hydroxyl group, having therefore the composition $CH_3 \cdot OH$. It was recognised in wood tar by Boyle as far back as 1661 and the composition was established by Dumas and Peligot in 1834. It does not occur naturally, but is produced in the steam distillation or dry distillation of most vegetable matter and to a certain extent by fermentation. On the large scale, it is prepared mainly by the destructive distillation of vegetable products, the chief source being wood, although the refuse from beet-sugar and other vegetable waste products is utilised to a certain extent. The commercial product thus obtained (described in next section) is submitted to repeated distillation to obtain the pure alcohol.

The great difficulty in purification is the removal of the few per

cent. of acetone usually present in the industrial product. T]
cannot be separated by simple distillation owing to the closeness
the boiling points, and chemical methods of separation have
be resorted to, such as chlorination of the acetone in order
raise the boiling point. Another indirect method is to ester.
the methyl alcohol, separate this from the acetone by distillati
and recover the alcohol by distillation of the ester with caus]
potash.

Recently a process of preparing methanol in a state of gre
purity by synthesis has been developed in France and Germany.

Sabatier and Senderens experimented many years ago on t]
synthesis of methyl alcohol by the hydrogenation of carbon monoxid
but without much success, probably owing to the fact that they we
working at too low temperatures and pressures. It has only be
with the development of high-pressure technique for catalys
gaseous reactions, as elaborated for the purpose of synthesisi
ammonia, that the production of synthetic methyl alcohol has be
possible. In 1921 R. G. C. Calvert [1] claimed to have convert
water gas into methyl alcohol up to 80 per cent. of the theoretic
yield. A patent taken out by Patart about the same time claimed
the production of methanol on a commercial scale by subjecting
mixture of hydrogen and carbon monoxide to a high pressure at
temperature of about 500° in the presence of a catalyst.

Patart's process,[3] proceeding from the established fact that zir
dust reacts with methanol vapour at a red heat to give carbo
monoxide and hydrogen in proportions substantially those of wat
gas, acted on the hypothesis that this action should be reversib
under high pressure. Experiments proved this to be the case, t]
compression of water gas to about 200 atmospheres at a temperatu
of over 400° in the presence of pure zinc oxide as a catalyst resulti
in a regular supply of synthetic methanol, according to the reactio
$CO + 2H_2 = CH_3 \cdot OH$.

The crude liquid thus obtained was greenish in colour an
distilled between 59° and 100°. This on re-distillation gave pract
cally pure methanol. The chemical engineering problems in t]
construction of the apparatus for this reaction were found to l
considerable, but the greatest difficulty to be overcome was t]
control of the process so as to secure quantitative conversion of t]
gases into methanol and avoid the waste caused by the mar
possible secondary reactions which result in the formation of fr
carbon, carbon dioxide, etc., as well as objectionable by-product
Patart was, however, able to overcome these difficulties and

particular to produce a product completely free from acetone, which is impossible except at great expense by the refining of wood alcohol.

A closely similar process formed the subject of patents taken out by the Badische Anilin- und Soda-Fabrik in 1923.[4] The improvements claimed in these over Patart's process mainly concern the complete purification of the reacting gases to prevent poisoning of the catalyst and the composition and structure of the catalyst so as to ensure the efficiency of the main reaction and prevent the setting up of those subsidiary reactions already referred to, which result in the formation of hydrocarbons and other impurities. The most important point revealed is the fact that it is necessary for the catalyst to be entirely free from iron or nickel. A certain amount of higher alcohols, such as butanol, is produced with the methanol and the process can be controlled within limits so as to yield a supply of these.

Operations under these patents were started towards the close of 1923 at Merseburg and developed on a large scale. The whole of the output until recently has been absorbed by the German dye industry, but as the production increases more and more is being exported at a price which shows a great advantage over the wood distillation product.

Other workers have devoted considerable attention to the synthetic production of methanol. Audibert claims,[5] for example, that methanol can be obtained, with a chemical yield of 100 per cent., by causing hydrogen to act upon carbon monoxide in the presence of the sub-oxides of Cr, Vd, Ur or Mo at a temperature of 250° and a pressure of 100 to 200 atmospheres.

A further process, in which methanol is produced by the hydrogenation of thymol, has been recently patented by the Camphor Manufacturing Co. of Düsseldorf.

Synthetic methanol is rapidly becoming a formidable competitor to the wood distillation product on account of the low price at which a pure product can be obtained.[6]

The pure alcohol is a colourless, mobile liquid, the smell of which is very faint and not unpleasant, resembling ethyl alcohol. The boiling point at normal pressure is 66°. According to Fuchs [7] it ranges from 65·06 at 710 mm. to 68·00 at 790 mm.

The melting point has been determined by several workers. Ladenburg [8] gives —94·9°, Van Nostrand [9] —97·1.

The specific gravity is 0·796. Klason and Norlin have determined accurately the sp. gr. of solutions of methyl alcohol in water of

varying strengths from 0 to 100 per cent. : their results are given in detail in a series of tables.[10]

Methanol burns with a pale blue flame and mixes with water in all proportions, also with alcohol and ether. It is closely similar to alcohol in its solvent properties.

It is obtainable practically pure on an industrial scale and is often marketed under various proprietary names, such as " Columbia Spirit." For use in the synthesis of dyes, etc., a very pure spirit is required, particularly freedom from acetone. Pure methyl alcohol is mainly employed for such chemical purposes rather than as a solvent, as the content of acetone in the cheaper wood alcohol is an advantage rather than otherwise for solvent purposes. It is employed for the introduction of the methyl group in the synthesis of perfumes and essential oils, synthetic drugs, etc.

Wood Alcohol.　(Wood Spirit, Wood Naphtha.)

The impure methyl alcohol used industrially as a solvent is known by these names in distinction to the pure product just described. This is prepared by the destructive distillation of wood : hard woods such as birch, oak, beech and elm are most satisfactory for the purpose and both the solid wood and sawdust are employed. In the case of the former, the wood is cut into laths about 4 feet in length and seasoned thoroughly for one or two years. If sawdust or chips are used they are moulded into briquettes or blocks before treatment.

The wood is first placed in a kiln maintained at a temperature of about 100° to drive off all residual moisture and sap. It is then loaded into the retorts, which are steel chambers of dimensions varying in individual works and provided with a large, tightly-fitting door for charging, which is fitted with an outlet pipe some 12 inches in diameter. The dried wood is loaded on to a steel trolley and run into the retort in the most progressive factories, but in some cases the older practice prevails of loading the wood into the retort direct, closely stacking it until the chamber is full, when the door is closed and the retort fired.

The vapour which comes off on heating is led through the outlet pipe into condensers. The worm condenser is not generally used in this case, but the reverse system of passing the gases into a chamber fitted with a number of tubes through which a constant circulation of cold water is maintained. The distillate is discharged from the condensing chamber into tanks, where it is allowed to settle and

separate out into tar and pyroligneous acid. This latter, which floats on the top, is a dark-reddish liquid with a peculiar penetrating odour and a strong acid reaction, running from 1·02 to 1·05 in density. It consists of acetic acid, methyl alcohol, acetone, allyl alcohols, phenols and other compounds.

The methyl alcohol, which is present to the extent of about 15 per cent., is separated by fractional distillation, the acetic acid being removed either by passing the distillate over calcium hydrate solution or treatment of the pyroligneous acid with lime prior to distillation. The crude wood alcohol thus obtained contains about 82 per cent. methyl alcohol with varying amounts of acetone, methyl esters, allyl alcohol, aldehyde, methylamine, etc. This is further distilled over lime to prepare the refined product, which contains about 95 per cent. methyl alcohol, the balance being mainly acetone.

Wood spirit is largely used as an adulterant for alcohol to render it undrinkable, on account of its poisonous nature, its cheapness and the difficulty of separation. It is an advantage for this purpose that it does not materially affect the properties of alcohol as a solvent and other purposes for which it finds industrial use. For this purpose, an impure spirit containing a high proportion of allyl alcohols and pyridine can be used.

Wood alcohol has the advantage of being a solvent for many inorganic substances and being freely miscible with water, as well as a solvent for fats, oils and soft resins. As previously mentioned, the proportion of acetone it contains assists it as a solvent and extracting agent.

As an extracting agent it is used in various industries in addition to paint and varnish manufacture. Nitrocellulose, for example, is refined by extraction with wood alcohol, and it is employed in the manufacture of other explosives.

Formic aldehyde is almost entirely prepared by the oxidation of wood alcohol, either by passing a mixture of the alcohol with air over a heated surface or by oxidation in presence of a catalyst. Commercial formic aldehyde usually contains about 10 per cent. of residual methyl alcohol.

Wood spirit is a good solvent for shellac and is largely employed in the preparation of spirit varnishes, insulating varnishes, hat polishes, shoe polishes, etc. Cheap lacquers for hardware are largely made with it. It is used as a detergent in laundry work. On the continent " esprit de bois " is used in place of methylated spirit as a household article, both as a fuel for use in spirit lamps, etc., and as a general cleaning agent.

It is extremely poisonous, much more so than ethyl alcoho as it is oxidised in passing through the system with formation formic aldehyde and formic acid. The pernicious practice drinking methylated spirit denatured with wood alcohol caus homicidal mania and is frequently fatal.

Alcohol. (Ethyl Alcohol.)

This is the hydroxide of ethane, having the compositi $C_2H_5 \cdot OH$. It is a substance of such widespread industrial impor ance that its technology had been fully investigated and sever works on the subject have been published which should be consult for detailed information.[11]

Alcohol is produced by fermentation whenever a ferment such yeast is allowed to act on sugar solutions of moderate strength temperatures between 50° F. and 90° F. In theory, the proce consists of a simple splitting up of the sugar into alcohol and carbo dioxide, but the actual reactions involved are far more complicated

In the fermentation of fruit juices for the production of alcohol liquors the ferment acts directly on the sugar present in the juic Alcohol for industrial purposes is, however, usually made fro cereals, in which the starch has first to be converted into sugar l the action of another organism in the process known as " malting and this is subsequently converted into alcohol by fermentati or " mashing." The fermented mass contains alcohol, water ar fusel oil, which is a mixture of higher alcohols, together with sm quantities of acetic acid, aldehyde and esters mixed with the sol and unfermentable portions of the original grain. The alcohol separated from this mixture by distillation.

Alcohol is also produced synthetically from calcium carbid The cycle of operations may be represented thus :—

Chalk, $CaCO_3$
(heated in the electric furnace with coal)
↓
Calcium carbide, CaC_2
(treated with water)
↓
Acetylene, C_2H_2
(Hydrated by dilute sulphuric acid)
↓
Acetaldehyde, CH_3COH
(reduced by hydrogenation)
↓
Alcohol, $C_2H_5 \cdot OH$

This is only a general indication of the synthesis, which has been carried out in many different ways and has formed the subject of innumerable patents.

A process for the production of synthetic alcohol from the ethylene contained in coke-oven gases has recently been introduced on an industrial scale in France.[12]

Absolute Alcohol is ethyl alcohol in a state of almost chemical purity, and, in particular, anhydrous. It is a colourless liquid almost without smell, very mobile, and having a strong burning taste. It boils at 78°, solidifies at −112° and has a specific gravity of 0·79. The refractive index has been determined as 1·3667.

It is decidedly hygroscopic, gradually absorbing moisture from the air unless kept tightly sealed. On the addition of water in small proportion combination takes place with considerable evolution of heat. It is prepared by dehydration of spirits of wine by re-distillation over quicklime and final treatment with metallic sodium.

The absolute alcohol prepared industrially as an analytical reagent, etc., usually contains a small quantity of water, from a half to one and a half per cent.

Absolute alcohol is made on an industrial scale in America by an improved method of distillation, which enables it to be prepared at a cost sufficiently low for industrial use as a solvent. It is claimed that the removal of the percentage of water contained in ordinary industrial spirit converts it into an active solvent for nitro-cellulose. It is, however, difficult to understand how this anhydrous condition can be maintained for any length of time in view of its pronounced hygroscopic nature.

Rectified Spirit of Wine (abbreviated S.V.R.) is the most concentrated alcohol obtained by distillation in the ordinary manner. It is " 60° over proof " and contains 90 per cent. of alcohol and has a specific gravity of 0·838. It is prepared from ordinary alcohol by diluting down to 45 to 50 per cent. with water and re-distilling in a " rectifying " still, *i.e.*, a still fitted with fractionating columns. Purification by treatment with wood charcoal is also employed. The process of purification is mainly a chemical one, in which the impurities are removed by oxidation.

Proof Spirit is a relic of the old days when the quality of alcohol was determined by pouring on to gunpowder and applying a light. If the proportion of water was sufficiently low the gunpowder would ignite, but if high the water would moisten it and prevent ignition. The spirit was classed as " proof " if it ignited and " under-proof "

if it did not. The composition of proof spirit as determined by thi
test was very arbitrary, but is now definitely determined by Act c
Parliament as a mixture of 49·24 per cent. by weight of alcohol (b
volume, the percentage of alcohol is 57·1) and 50·76 per cent. watei
with a specific gravity of 0·920.

A spirit is known as so many degrees over-proof or under-prooc
according as it contains a higher or lower percentage of alcohol tha
this standard. The percentage of water can be determined accuratel
by taking the specific gravity. A special form of hydrometer i
usually used, graduated to read directly in degrees proof, but th
specific gravity can be taken in the usual way and the compositio
found from the tables which are published in all standard works o
alcohol and chemists' pocket-books.

Methylated Spirit (Denatured Alcohol).—This is spirit of no
less than 50 over-proof adulterated for industrial use with som
noxious substance so as to render it unfit for drinking and free it fror
excise duty. It is essential for the purpose that the added substanc
should not interfere with the use of the spirit as a solvent and fo
household purposes as a fuel, cleaning agent, etc. Wood naphth
in the proportion of 10 per cent. was originally used, but as this wa
easily removed by distillation and, moreover, certain persons coul
not be prevented from drinking it, with serious results, three-eighth
of 1 per cent. mineral naphtha was added. The regulations for it
composition have been altered from time to time to ensure renderin
it undrinkable and at the same time as far as possible non-poisonou
Since June 1918 the addition of a small quantity of methyl-violet
1 oz. to 4,000 gallons, has been required in order to provide a furthe
safeguard by giving it a distinctive colour.

Since May 1924 the use of crude pyridine prepared from bone oi
has been legalised as the denaturant. This substance has been use
as the denaturant on the Continent and in the United States fo
some years.

The general composition is given by Simmonds [13] as :—

Ethyl alcohol	83·05
Methyl alcohol	7·73
Ketones (calculated as acetone)	1·02
Esters (calculated as methyl acetate) . . .	0·13
Unsaturated compounds (such as allyl alcohol) .	0·08
Pyridine	0·02
Mineral naphtha	0·38
Water	9·21

Methylated Finish is methylated spirit in which is dissolved a proportion of rosin in order to enable it to be sold without a licence. It must contain not less than 3 oz. to the gallon to pass the Excise.

Industrial Spirit is the grade used as a solvent for manufacturing purposes. It is denatured in a similar manner to methylated spirit in order to prevent its use for drinking and allow it to be used free of duty, but the denaturing is not carried to such an extent, to avoid interference with its technical properties. It is not allowed to be sold for general use, but is restricted to manufacturing purposes only and controlled by licence. Great Britain was one of the first countries to introduce this denatured alcohol and exempt it from duty, for use as an industrial solvent.

It differs from ordinary methylated spirit in three respects :—

1. The petroleum spirit is absent.
2. It contains only half the quantity of wood naphtha.
3. The colouring indicator is omitted.

The average composition, as given by Simmonds,[13] is :—

Ethyl alcohol	87·92	per cent.
Methyl ,,	3·87	,,
Ketones (acetone)	0·51	,,
Esters (methyl acetate)	0·06	,,
Unsaturated alcohols	0·04	,,
Pyridine	0·01	,,
Water	9·21	,,

The restrictions placed on the use of this spirit are that it cannot be sold by retailers, but must be obtained by consumers direct from the manufacturers in quantities of not less than 5 gallons at a time. Manufacturers must first obtain a permit from the Excise authorities, stating the purpose for which it is intended to be used, and a register of its consumption must be kept available for inspection by the Excise authority. Regulations are also made as to its storage in factories, to safeguard against fire.

Ordinary industrial alcohol has a specific gravity of 0·815 to 0·820 and a boiling point of 78°. The flash point is 57° to 60° F.

Alcohol acts as a solvent for both organic and inorganic substances, being one of the few solvents which are miscible in all proportions with both water and organic liquids. It dissolves

oleo-resins and balsams and the turpentines obtained from thei
with the exception, according to Cuénot, of that from Gurju
balsam.[14]　It dissolves rosin, mastic, gamboge, Dragon's Blood ar
similar resins and some of the semi-fossil resins such as Manilla, bu
not the harder resins such as Copal and Kauri.　It is one of the fc
solvents for Shellac, but only dissolves it partially, giving a turbi
solution.　It is the principal solvent for the synthetic resins both c
the coumarone and phenol-aldehyde type.　The latter class ᵃarᵢ
however, only soluble when partially polymerised and become quit
insoluble if the reaction is carried to completeness.

It mixes freely with the aromatic hydrocarbons benzene, toluene
etc., and dissolves naphthalene, but not its hydrides (cf. page 46,
It does not dissolve petroleum hydrocarbons, but readily dissolve
their fatty acids and the soaps prepared from them.　The vegetabl
oils, or glycerides of the fatty acids, such as linseed, poppy and Chin
wood oils, are quite insoluble, but an exception is found in castor oi
which is freely soluble.　It dissolves many organic substances whic
are soluble in water and also many inorganic compounds, such a
potassium and sodium hydroxides.

Industrial alcohol does not dissolve cellulose nitrates or celluloi(
although it is claimed that these are soluble in absolute alcoh(
(cf. page 91).　In the paint and varnish industries alcohol is mainl;
used as a solvent for shellac and soft resins in the preparation o
spirit varnishes, lacquers and French polishes.　It is employed in ɛ
wide range of industrial chemical reactions, also as an illuminant anc
as a fuel and motor spirit.

Solidified Alcohol is a solution of sodium stearate in methylatec
spirit (or wood spirit on the Continent).　The soap is made b;
saponifying stearin with caustic soda.　This is melted and dis
solved in sufficient spirit to set into a soft, gelatinous mass oi
cooling.

Specification.—Industrial alcohol for use in the manufacture o
aeroplane dope must comply with the following requirements [15] :—

1. A clear, colourless liquid containing 5 per cent. of wooc
naphtha.

2. *Specific Gravity*—Not less than 0·817 at 15° (*i.e.* 66 over-proof).

3. *Distillation Range.*—95 per cent. between 76° and 79°.

4. *Volatile Residue*—Not more than 0·01 per cent.

5. *Acidity.*—2 Drops $N/10$-caustic soda must neutralise 10 c.c.

6. *Alkalinity.*—Not more than 0·02 per cent. by weight.

7. Must give a clear solution with distilled water in all proportions

heAlcohol Group*

Propyl Alcohols.

Propane, C_3H_8, is capable of forming two isomeric alcohols having the composition represented by the formula $C_3H_7 \cdot OH$. The *normal alcohol* is contained in potato fusel oil and obtained from it by fractional distillation.

Iso-propyl alcohol is obtained by the hydrogenation of acetone in presence of a catalyst. A pure alcohol is prepared by this process in Germany under the name Persprit.[16] It is also prepared in America from propylene by treatment with sulphuric acid to give the sulphate, which is then hydrolysed.[17]

Both these alcohols are closely similar to ethyl alcohol in their properties and are freely soluble in water. The solvent power is rather greater than that of alcohol and the physiological effect is similar. They differ from alcohol chiefly in their physical constants, which are as follows :—

	Normal.	Iso.
Specific gravity......	0·804	9·790
Boiling point.........	97·4	82·7

They are not employed to any great extent as solvents.

They are mainly used in the preparation of fruit essences, perfumes and cosmetics, and as substitutes for alcohol, as they are not subject to specific duty on importation or manufacture in this country, and there are no Revenue regulations governing their composition and use.

Butanol, or Butyl Alcohol.

Theoretically four alcohols can be derived from butane, C_4H_{10}, having the formula $C_4H_9 \cdot OH$.

All these isomers have been known for some time and their constants determined as follows :—

Normal butyl alcohol	.	boiling point	117°	sp. gr.	0·810
Iso-butyl alcohol	.	,, ,,	108°	,, ,,	0·800
Secondary butyl alcohol	.	,, ,,	99°	,, ,,	0·827
Tertiary butyl alcohol	.	,, ,,	84°		

With the exception of the secondary alcohol they are present in small quantity in fusel oil.

The normal alcohol is the most important of these. It wa prepared originally from butyl aldehyde or butyric acid. Con mercial butyl alcohol, or butanol, consists essentially of the norma alcohol of a high degree of purity. Its production on an industri scale is of quite recent introduction.

In the course of researches on the production of synthetic rubbe the need for butyl alcohol in large quantities became apparent an its production by fermentation was suggested. Fernbach, in cor junction with Weizmann, isolated a bacillus which would produc butyl alcohol from potatoes and a patent was taken out for th process in 1912. The process was, however, difficult to work, as required for its growth strictly anaërobic conditions in closed vessel The operation of this process was very limited, as Fernbach's bacillu would only operate on starchy materials such as potatoes, and coul not be cultivated in cereals, which limitation rendered the produc costly. Subsequently Weizmann, working on maize as a ra material, succeeded in isolating a further bacillus which, workin in a " mash " of practically any cereal, can be successfully cult vated under either aërobic or anaërobic conditions, thus greatl facilitating the application of the process under industrial condition This process is described in a patent taken out in 1915.[18]

Weizmann commenced by inoculating sterilised maize mas with the bacillus, the temperature of the culture being maintaine at a temperature of 90°—100° for a period of 4 to 5 days. A number— about one hundred—of such cultures were prepared, and from thes were selected those showing the most vigorous fermentation. Thes selected cultures were then heated to 90°—100° for 1 or 2 minutes with the result that the weaker bacteria were killed and only th more resistant spores remained alive. By repeating this proces many times on the principle of the " survival of the fittest," a strai of highly active and resistant bacteria was developed, which wa used to inoculate sterilised maize on a large scale and develop fermen tation by their growth with the resultant formation of acetone, ethy alcohol and higher alcohols, principally butyl. In a general way the process thus resembles that of the production of ethyl alcoho by the fermentation of grain, and existing plants for the productio of alcohol could be readily adapted to this process.

The fact that acetone was produced as one of the products o these fermentation processes had been discovered by Strange an Graham some time previously. This suggested the utilisation o the process as a means of supplying the huge and pressing deman for acetone during the war.

Dr. Weizmann, after developing this process, handed it over to the Government, and after perfecting it commercially it was first operated on an industrial scale at a distillery equipped for the purpose in Toronto. When America came into the war two existing distilleries at Terre Haute, Indiana, U.S.A., were purchased jointly by the British and American Governments and re-fitted for this process on a large scale. During the war acetone was the main objective, the butyl alcohol being a by-product of little industrial importance. At the close of the war the Allied Governments consequently had accumulated large stocks of butanol available for industrial use. Investigation soon revealed its value as a solvent in many industries, with the result that the plants were purchased from the Government by a syndicate with the object of developing the process with butanol as the main objective. The production developed rapidly to important dimensions. The consumption in 1924 was approximately 3,000,000 gallons.

The fermentation process, as carried out on an industrial scale, is operated in four stages :—

1. *The Preparation of Sterilised Mash.*—The raw material for this is maize. This is ground into flour, mixed with water in the proportion of 15 parts of water to 1 part of flour and cooked under pressure in closed tanks fitted with stirring gear. This operation takes from 3 to 4 hours, the temperature being regulated at 130° to 140° at a pressure of 2—3 atmospheres. The sterilised mash thus produced is then cooled to about 35° and run into the fermentation vats.

2. *Production of the Culture.*—This is prepared in the manner described above, the pure culture obtained in the laboratory in the first instance being used to inoculate successively larger and larger quantities until it is available on an industrial scale.

3. *Fermentation.*—The mash having been transferred to the fermentation vats, which are closed steel tanks of about 50,000 gallons capacity, it is inoculated with the culture, and fermentation commences after about 5 to 10 hours. The action proceeds vigorously for about 36 hours and then falls off rapidly as the starch becomes used up, reaching completion in about 48 hours. The operation requires considerable skill and experience to carry out successfully. It is necessary to maintain the steady propagation of the bacteria and prevent contamination by other bacteria which would impair the efficiency of the fermentation. Any interference with the proper conditions may cause the entire stoppage of the process owing to the poisoning of the bacteria. An accident of this description

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occurred in 1923, with the result that the entire production of buta
was practically stopped for some months.

During fermentation, carbon dioxide and hydrogen are evol
in large quantities and a fermented mass is developed which conta
approximately 20 lb. of combined solvents for each hundredwei
of flour used, the remainder of the mash being unfermented resi
mixed with water.

The composition of the crude product thus obtained varies c
siderably. A sample examined by the author contained :—

> Butyl alcohol . . . . . 56 per cent.
> Acetone . . . . . . 32 ,, ,,

the remaining 12 per cent. consisting of ethyl alcohol, hexyl and ot
higher alcohols, with a small proportion of fatty acids.

4. *Distillation.*—The crude solvent is separated from the resic
by running through a beer still and is then subjected to count
current distillation with live steam. The crude distillate tl
obtained consists approximately of 50 per cent. combined solve.
and 50 per cent. water.

This is then separated by fractional distillation into (1) aceto
(2) ethyl alcohol, (3) crude butanol, (4) residual " Yellow Oi
containing hexyl alcohol and other higher alcohols.

The crude butanol is a brownish-red liquid containing abc
80 per cent. butyl alcohol and about 12 per cent. of water, the balai
consisting of traces of acetic acid and other alcohols such as proj
and amyl. This is re-distilled in a continuous distillation a
separation plant to yield the refined commercial butanol, which
a water-white liquid of approximately 98 per cent. purity.

Butanol is produced in France by the same fermentation proce
In Germany, large quantities are also produced by the carbi
process in conjunction with acetone (see page 108), being form
from the acetaldehyde by conversion into crotonaldehyde, thei
to aldol, which on hydrogenation gives butanol. It is also produc
to a limited extent as a by-product in the preparation of methai
by the water-gas process (see page 87). By varying the cataly
and regulating the physical condition the resulting product can
varied within limits to contain more or less of the higher and low
alcohols according to the demand. The production of butanol
this process, however, does not exceed at most 10 per cent. of t
methanol produced.

Properties.—Commercial butanol is a clear water-white liqu

with a peculiar penetrating odour which has a characteristic effect when inhaled, generally described as "gripping the back of the throat." Like all the alcohols, it has considerable toxic effect and produces distressing symptoms if inhaled for any considerable time. Its composition is 98 per cent. butyl alcohol, the balance being traces of ethyl alcohol and acetone. It is practically anhydrous, the usual specification on this point being that it shall show no cloudiness when mixed with benzol in the proportion of 1 volume of alcohol to 19 volumes of benzol. The boiling range is 110° to 118°; a good sample will give the following result :—

Under 110°	.	.	.	.	nil.
110°—114°	.	.	.	.	10 per cent.
114°—118°	.	.	.	.	90 ,, ,,
Over 118°	.	.	.	.	nil.

The flash point is 97° F. (36° C.), and the specific gravity is 0·810.

Unlike the lower alcohols, butanol is not miscible with water in all proportions, but is only soluble to the extent of 1 part of butanol to 12 parts of water. The solubility at different temperatures is given in the following table :—

0°	.	.	10·3 per cent.	60°	.	.	6·3 per cent.
10°	.	.	9·0 ,, ,,	70°	.	.	6·5 ,, ,,
20°	.	.	7·7 ,, ,,	80°	.	.	7·0 ,, ,,
30°	.	.	7·1 ,, ,,	90°	.	.	7·7 ,, ,,
40°	.	.	6·5 ,, ,,	100°	.	.	9·0 ,, ,,
50°	.	.	6·3 ,, ,,	110°	.	.	10·8 ,, ,,

It will be seen from this that it decreases steadily with rise of temperature from freezing point to a minimum at 50°, after which it rises in the same proportion with further increase of temperature.

Butanol is miscible in all proportions with ether, alcohol, chloroform, acetone and esters. It is an active agent for promoting the solubility of other liquids. Thus the addition of 3 per cent. of butanol enables benzene and alcohol to mix in all proportions. It is practically neutral, the acidity, calculated as acetic acid, not exceeding 0·02 per cent. It is free from aldehyde and chlorides. On oxidation it yields butyric acid.

It is one of the few materials which act as a solvent for all types of resins. It dissolves both shellac, soft resins like damar and Manilla and hard resins like Congo. It also dissolves synthetic resins

both of the coumarone and phenol-aldehyde types, provided t]
latter have not been polymerised too far.

As it is also a solvent for all types of oil, its use in the preparatio
of spirit varnishes enables drying oils to be used as plasticise
to increase the elasticity of the film, instead of resorting to no
drying oils such as castor oil, which are soluble in the lower alcoho]

By the solution of hard resins in mixtures of alcohol and butano
spirit paper and stoving varnishes can be prepared which give a mu
harder and tougher film than those prepared in the usual manner fro
soft resins. It has a further advantage as an ingredient of spi
varnishes of retarding the rate of evaporation. The rapid evapor
tion of alcohol causes two difficulties in practice. In the first plac
the viscosity of the varnish increases so rapidly when it is sprea
on the surface as to cause it to dry in the brush, particularly
warm weather, the varnish commencing to set before it can flow o
with a smooth film, with the result that the brush marks are n
properly eliminated and an uneven surface is produced.

The second difficulty referred to is that known as " blushing
Not only does the industrial alcohol used in spirit varnishes conta
a decided percentage of water, but it is hygroscopic and inclines
increase its content of water on storage. When the varnish ma
with it is spread on to a surface the rapid evaporation of the alcoh
absorbs a considerable amount of heat, with the result that t]
temperature of the varnished surface is lowered to such an exte
that this water content cannot evaporate readily and remains on t]
film, giving it a milky appearance. The more rapid the evaporatio
the greater the lowering of the temperature produced. In extren
cases where the air is already saturated with moisture this lowerir
of the temperature by the evaporation of the solvent is sufficient
cause actual condensation of moisture from the surrounding air on
the surface.

The addition of butanol in the proportion of about 10 to 20 p
cent. to the alcoholic thinner, owing to its much slower rate
evaporation, retards the evaporation of the alcohol sufficiently
remedy both these defects. It slows down the drying sufficient
to allow the varnish to flow to an even coat and also to allow t.
moisture to absorb the heat necessary for vaporisation.

Butanol, although not itself a solvent of nitro-cellulose, is us
in a similar manner in cellulose lacquers. It is added in small pr
portion to the thinner to retard the evaporation of the low-boili
solvents, which have a tendency to cause " blushing " of the fi]
under favourable conditions of humidity by precipitating moistu

from the air, which reacts with the nitro-cellulose, giving the film a milky appearance. Its addition also causes the film to flow out smoothly and prevents pinholing and similar defects.[19]

In addition to its solvent power for resins and oils, butanol is also a powerful and rapid solvent for linoxyn and other oxidised oil films. On this account it forms a very effective ingredient of paint removers. Its comparatively slow evaporation is an advantage from the practical point of view, whilst its high flash point renders it more safe in use than equally effective solvents like acetone, which on this account are subject to transport restrictions. Unfortunately, its value for this purpose is discounted to some extent by its irritating effect on the throat, which makes it difficult to work with in confined spaces.

This solvent action on linoxyn may also be taken advantage of by adding a small proportion of butanol to certain types of enamels which have a tendency to skin badly in a partly-filled can. The butanol evaporates into the air space in the can and by keeping the oxidised oil in solution as it forms, prevents the skin from developing.

Nelson and Wein [20] have found that butanol is the most effective solvent for the metallo-organic compounds used as driers, such as zinc and lead linoleates, resinates and tungates. This suggests its use for the preparation of the liquid driers now largely employed in the paint industry, as the metallic soaps have a well-known habit of dropping out of solution on keeping when prepared in the ordinary way with turpentine or petroleum solvents.

Another use for which butanol has been employed is as an ingredient of rust-removing solutions for ironwork. A mixture of butanol and phosphoric acid is used largely for this purpose. The phosphoric acid is the active agent in removing the rust in the mixture, the function of the butanol being to act as a solvent for grease, etc., and clear the surface for the acid to operate.

Specification.—B.E.S.A., D 17, June 1918 (see page 140), gives the following data for butanol for use in the manufacture of aeroplane dope :—

Specific Gravity.—0·810 to 0·820 at 15°.
Distillation Range.—95 per cent. 95°—120°.
Residue.—Not more than 0·01 gr. per 100 c.c.
Acidity.—Not above 0·01 per cent. calculated as acetic acid.
Alkalinity.—Not above 0·01 per cent. calculated as NaOH.
Purity.—Not less than 94 per cent. butyl alcohol, determined by Verley and Bölsing method (page 106).

Amyl Alcohol.

Pentane, C_5H_{12}, is capable of forming eight isomeric alcohol having the formula $C_5H_{11}\cdot OH$. A mixture of these, in which th predominant member is iso-amyl alcohol, is obtained by the disti lation of fusel oil. This alcohol was first extracted from the spir obtained by the fermentation of substances containing starch, hen the name amyl (from *amylum* — starch).

Fusel Oil is the residue obtained from the rectification of alcoho containing all the higher alcohols, etc., produced in the fermentatio It is a body of extremely complex composition which varies co siderably according to the grain used for the fermentation. It produced to the extent of about 0·5 per cent. in ordinary alcohol fermentation.

The following gives an indication of the composition from tw different sources, according to K. Windisch [21] : —

	Percentage by weight.	
	Potato.	Grain (ryo).
Normal propyl alcohol	6·85	3·69
Iso-butyl alcohol	24·35	15·76
Amyl ,,	68·76	79·85
Hexyl ,,	— —	0·13
Heptyl ,,		trace
Free fatty acids	0·01	0·16
Fatty acid esters	0·02	0·30
Furfural and bases	0·005	0·02

The supply of amyl alcohol is dependent on the quantities of th fusel oil available from the alcohol distilleries and is consequent limited and at times not equal to the demand. The principal supp is derived from the potato spirit obtained as a by-product in th manufacture of whisky.

Amyl alcohol is obtained from the crude fusel oil by shaking wi slightly alkaline water to remove the ethyl alcohol. This is allowe to stand, when the amyl alcohol separates out on top of the lye. Th is drawn off, dried over calcium chloride and re-distilled. Th refined product is still a mixture of alcohols, the approximate cor position being : —

Propyl alcohol	.	.	.	.	7 per cent.
Iso-butyl alcohol	.	.	.	.	24 ,, ,,
Amyl alcohol	.	.	.	.	69 ,, ,,
Fatty acids, furural, etc.	.	.	.	traces.

It may contain ethyl alcohol in addition, and the Excise regulations allow 15 per cent. as a normal proportion and admit it duty free up to this limit. Being thus a mixture of alcohols of which only the amyl content is practically anhydrous, it generally contains a few per cent. of water.

Amyl alcohol is also prepared synthetically by various processes, usually starting with petroleum spirit or a similar hydrocarbon. These are chlorinated and then treated with an acetate. The synthetic product Peramyl alcohol is a mixture of higher alcohols obtained in this way, having a distillation range from 90° to 160°, and a specific gravity of 0·883.

Pure amyl alcohol can be prepared by treating a mixture of ethyl valerate and absolute alcohol with sodium, adding the latter gradually in small pieces, heating the mixture over an oil bath for 2 or 3 hours and fractionating. The distillate is then dried over potassium carbonate and re-distilled.[22]

Commercial amyl alcohol is a colourless, oily liquid with a smell closely resembling that of butyl alcohol, and the same curious effect on the throat. The boiling point is 121° to 131° and the specific gravity 0·825.

It is only slightly soluble in water, 1 volume being soluble in 39 volumes of water. It mixes freely with other alcohols, and in its solvent power is equivalent to butyl alcohol. Its toxic effects are rather more pronounced than with butyl alcohol, inhalation of the vapour being poisonous. The toxic effects of drinking inferior spirits are mainly due to the presence of amyl alcohol.

It is largely used as a solvent for natural and synthetic resins and for the preparation of amyl acetate for the manufacture of cellulose lacquers, etc. On account of the uncertainty of the supply and the variability of its composition it is, however, now largely replaced by butyl alcohol, which has the advantage of being of constant composition.

Di-acetone Alcohol.

This is a synthetic alcohol formed by the condensation of two molecules of acetone by the transference of one hydrogen atom from a methyl group in one molecule to unite with the oxygen in the other molecule thus :—

$$O = C{<}^{CH_3}_{CH_3} \qquad\qquad O = C{<}^{CH_3}_{CH_3}$$

Two molecules of Acetone.

$$O = C{<}^{CH_3}_{CH_2}{-\!\!-\!\!-\!\!-\!\!-}^{HO\diagdown}{}_{}C{<}^{CH_3}_{CH_3}$$

One molecule of Di-acetone alcohol.

It was first prepared by Heintz in 1873 [23] by distilling acetone ove concentrated solution of potassium hydroxide. Numerous otl investigators prepared it subsequently by different methods, a several patents have been taken out for its manufacture on a co mercial basis, the main principle employed being that of passi acetone over a catalyst such as granular calcium hydroxide.[24]

Di-acetone alcohol is a water-white liquid miscible in all prop tions with both water and alcohol, and also miscible with beni up to 50 per cent. It has a boiling point of 163°, and a speci gravity of 0·910 to 0·930.

It contains a small proportion of unaltered acetone, and also trace of acetic acid, but the acidity should not exceed 0·02 per cei It is used to a considerable extent as a solvent in the United Stat< One of its principal uses is for the making of nitro-cellulose solutio for stiffening leather in the boot industry, but it is also used in t preparation of cellulose varnishes, being a good solvent both f cellulose and resins. It is, in fact, closely similar in solvent properti to methyl ethyl ketone, but has a considerably slower rate evaporation.

Benzyl Alcohol.

This is the alcohol derived from toluene, thus :—

Toluene.   Benzyl alcohol.

It was originally obtained from Peruvian balsam by extraction wit caustic potash, but is generally prepared synthetically. The usu< method of preparation is to treat toluene with chlorine gas an saponify the benzyl chloride thus formed by digestion with causti soda. It is also prepared by boiling benzaldehyde with causti soda.

Benzyl alcohol is used to a certain extent as a solvent, mor particularly for cellulose acetate dopes. For this purpose it i required to pass the following specification :— [25]

Specific Gravity.—1·050—1·055 at 15°.

Initial Boiling Point.—Not below 200°.

Distillation Range.—95 per cent. 200°—210°.

Residue.—Not more than 0·1 per cent.

Free Acid.—Not more than 0·1 per cent. (calculated as benzoic acid)—hydrochloric acid must be absent.

Chlorine Content.—Must not exceed 0·05 per cent. by weight. The test specified is to boil with alcoholic potash, acidify with nitric acid and precipitate with silver nitrate.

Purity.—Not less than 97 per cent. determined by Verley and Bölsing method (page 106).

Hexalin, or Cyclohexanol.

This is the monatomic alcohol derived from cyclohexane and is prepared by the hydrogenation of phenol, thus :—

Phenol, $C_6H_5 \cdot OH$ Cyclohexanol or Hexalin, $C_6H_{11} \cdot OH$.

The process of preparation is closely similar to that of Tetralin, and it is, in fact, produced by the same plant. As in the case of the naphthalene hydrides described in Chapter II, the hydrogenation results in a lowering of the boiling point and specific gravity :—

		Boiling point.	Sp. gr.
Phenol.	Crystalline solid	181°	1·084
Hexalin.	Heavy liquid	160°	0·945

There is a similar change in other properties—the characteristic odour of phenol, and phenolic characteristics, such as solubility in alkalies, and the pronounced acid and corrosive action, which give phenols such powerful antiseptic qualities, disappear. Hexalin is quite neutral in character and has properties similar to those of an alcohol of high molecular weight.

These hydrogenated phenols have found many industrial uses on account of their powerful solvent and emulsifying properties. One of their chief uses is in soap manufacture, as they form a clear solution with aqueous soap solution and increase the detergent properties owing to their solvent action on oils and fats.

Dr. Hueter [26] states that excellent results have been obtained by adding from 10 to 20 per cent. of hexalin to the fats before saponification.

Hexalin is used not so much as a direct solvent as for promoting the solubility of substances in other organic solvents and for lowering

the surface tension between two liquids so as to render them misc[...]
Thus a recent German patent [27] describes the use of hexali[...]
combination with alkaline oleates; this preparation, added
liquid hydrocarbons, renders them soluble in water or capabl[...]
forming a stable emulsion with water. A similar action occurs [...]
the hydrocarbon chlorides (see page 132).

Although hexalin does not itself dissolve celluloid but me[...]
softens it, if a small quantity of hexalin is added to a solutio[...]
celluloid in amyl acetate a much more stable solution is formed wl[...]
can be diluted in any proportion with benzol or white spirit with[...]
precipitation.

Methyl Hexalin.

The name Heptalin was originally used for this substance,
has been discontinued to avoid confusion with Hexalin.[26] It b[...]
the same relation to hexalin as toluene to benzene, having
formula :—

$$
\begin{array}{c}
H \\
H\diagup\!\!\!\diagdown\ H\text{-}CH_3 \\
H\diagdown\!\!\!\diagup H\text{-}OH \\
H
\end{array}
$$

It is prepared by hydrogenating o-cresol. It is an oily liq[...]
with a rather unpleasant odour which is not strong but very [...]
sistent. The boiling point is 170°—180°, and the specific grav[...]
0·930. Methyl hexalin is closely similar to hexalin in its propert[...]
but not quite so powerful in its action. It is, however, considera[...]
cheaper to produce and therefore takes the place of hexalin [...]
most industrial purposes.

Determination of Alcohols by Verley and Bölsing's Method.

1 to 2 Grams of the liquid are weighed into a 200 c.c. flask, a[...]
to this is added 25 c.c. of the following mixture :—

Pure acetic anhydride . . .	12 per cent.
Pure pyridine	88 ,, ,,

The flask is then fitted with a reflux condenser and digested o[...]
the water-bath for 15 to 30 minutes. It is then cooled, 25 [...]
distilled water added, and titrated with $N/2$-caustic soda, usi[...]
phenol phthalein as an indicator. The amount of the alcohol [...]
calculated from the amount of acetic acid found, according to
molecular weight, one molecule reacting to form one molecule
acetic acid.

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CHAPTER V

KETONES AND ETHERS

KETONES are a group of organic compounds closely similar to th
aldehydes, resulting from the oxidation of secondary alcohols; the
are intermediate, in fact, between the alcohols and the fatty acid.
The lower members of the series are neutral and highly volatil
liquids of characteristic odour. With increasing complexity the
become insoluble in water and the melting point rises, the highe
members being solid and odourless.

Acetone.

This is the most important member of the ketone group and ha
the composition di-methyl ketone :—

$$\begin{matrix} CH_3 \\ \\ CH_3 \end{matrix}\Big\rangle CO.$$

It was discovered early in the nineteenth century and investigate
by Liebig and Dumas in 1832. It is formed in various ways, suc
as by the oxidation of alcohols, the distillation of the calcium salt
of fatty acids, or the decomposition of organic chlorine derivatives

Acetone has been employed industrially as a solvent for man
years and is used in large quantities. Numerous processes for pre
paring it on a commercial scale have been introduced from time t
time, but substantially the whole of the acetone available is no
prepared by the following three methods :—

1. *The Wood Distillation Process.*—The raw material in thi
process is acetate of lime, produced by saturating lime with th
pyroligneous acid produced by the distillation of wood. This is dr
distilled, when it splits up according to the reaction :—

$$Ca(CH_3 \cdot COO)_2 = CaCO_3 + (CH_3)_2CO.$$

The reaction is not quantitative, a good deal of loss occurring throug
subsidiary reactions unless the distillation is carefully controlle
and the heating kept uniform. The crude distillate is a viscou
liquid of complex composition, from which the acetone is obtaine
by distillation, the residue being acetone oil (see page 111).

2. *The Carbide Process.*—Acetone is formed as a subsidiary pro
duct in the manufacture of acetic acid from calcium carbide. Th
steps in the production by this method are represented diagram
matically thus :—

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Calcium carbide, CaC$_2$
on addition of water decomposes, giving

↓

Acetylene, C$_2$H$_2$
by combination with elements of water yields

↓

Acetaldehyde, CH$_3$·COH
polymerises to

↓

Metaldehyde, (CH$_3$·COH)
on oxidation forms

↓

Acetic Acid, CH$_3$·COOH

↓

by removal of carbon dioxide and water condenses to

↓

Acetone, (CH$_3$)$_2$·CO

This process produces a very pure acetone, but it is expensive to work. It is largely operated in Germany.

3. *The Fermentation Process.*—Acetone is formed as a by-product in the production of butyl alcohol by the fermentation of grain (see page 96). The operation of this process to supply the demand for butyl alcohol and derivatives has resulted in the production of acetone in large quantities and it has now become one of the principal sources of supply.

Acetone is obtainable in a state of great purity, a good sample showing 99 to 100 per cent. of dimethylketone. It is a mobile liquid perfectly clear and water-white with a mild and not unpleasant odour. A good sample should be practically anhydrous, and show no turbidity with distilled water and no residue on evaporation over the water bath. It should be free from aldehydes and unsaturated by-products; this is usually determined by the *permanganate test*, in which 100 c.c. of the acetone are mixed with 1 c.c. of a 0·1 per cent. solution of potassium permanganate and kept at 15°. The presence of such impurities is indicated by a rapid discharge of the pink coloration, which should persist in a pure sample for half an hour at least. The specific gravity is 0·792 to 0·799 at 15°, and the boiling point 56°. A good sample will distil completely within 2°. It is extremely volatile and inflammable and flashes at ordinary atmospheric temperature, the Flash Point being well below 0°. It mixes with water and alcohols in all proportions and with all other organic solvents. It can be salted out from its solution in water by the

addition of calcium or sodium chloride. The strength of a soluti
of acetone in water is indicated by the specific gravity of the soluti
as shown in the following table :—

Acetone, per cent.	Sp. gr. at 20°.	Acetone, per cent.	Sp. gr. at 20°.
100	0·7920	86	0·8331
99	0·7951	85	0·8359
98	0·7982	84	0·8387
97	0·8013	83	0·8415
96	0·8044	82	0·8442
95	0·8075	81	0·8470
94	0·8114	80	0·8498
93	0·8133	75	0·8613
92	0·8162	70	0·8755
91	0·8191	65	0·8875
90	0·8220	60	0·8995
89	0·8248	55	0·9103
88	0·8276	50	0·9205
87	0·8303		

The solvent power is extremely great and covers a very wi
range of substances. All animal and vegetable oils are soluble
all proportions and all essential oils. Mineral oils are, however, or
slightly soluble. It is one of the few solvents for the linoxyn form
by the " drying " of vegetable oils. Rosin and soft resins a
completely soluble and hard and fossil resins are soluble to a gre
extent, although not completely. Shellac is soluble to the extent
over 80 per cent. Synthetic resins are not, however, soluble
acetone. Gums are only slightly soluble. According to R.
Reuber,[1] the percentage of various pitches and waxes dissolv
by acetone is as follows : —

Coal-tar pitch	.	.	70	Beeswax	.	.	.	94—9
Gilsonite	.	.	25	Carnauba	.	.	.	36
Syrian asphalt	.	.	6	Ozokerite	.	.	.	69
Trinidad pitch	.	.	42	Candellila	.	.	.	99·8

With the exception of amyl and butyl acetates, acetone forms t
most active solvent for cellulose esters. Cellulose nitrate, acetate an
celluloid are all freely soluble, and it is employed largely in t
preparation of cellulose varnishes and lacquers and the manufactu
of aeroplane dopes.

On account of its great solvent power for resins and oxidise
oils, acetone forms one of the principal ingredients of most neutr
paint removers. It softens a hardened film of paint and varnish wi
great rapidity, but its value in this connection is somewhat restricte
by its extreme volatility, the surface hardening again in the course

ketones and ethers

a few minutes unless it is operated upon immediately after application of the solvent.

It is largely used as a solvent for cellulose in the manufacture of explosives such as cordite, artificial silk and celluloid. It is employed in many other industries as a solvent and extracting agent. It forms the raw material for the production of many other organic compounds, notably chloroform and iodoform. It is also used largely in the laboratory as a solvent and extracting agent. In the analysis of varnishes Morrell[2] has described a method of separating polymerised oil from ordinary refined linseed oil by means of acetone.

Determination of Acetone by Messinger's Method.—To 50 c.c. of distilled water add 5 c.c. of the solution to be tested and make up to 100 c.c. with distilled water, shaking thoroughly. This will give a 5 per cent. solution. Place 5 c.c. of double normal solution of soda hydrate in a 200 c.c. flask, and add exactly 1 c.c. of the 5 per cent. solution mentioned above from a pipette, keeping the end of the pipette below the surface of the soda solution. Shake gently and add slowly from a pipette 25 c.c. of $N/10$-iodine solution. Shake the flask whilst the iodine is being added, and allow to stand for 5 minutes in the dark. Then add 5 c.c. of dilute sulphuric acid, 1 part acid to 4 parts water. This liberates the free iodine, which should then be immediately titrated back with $N/10$-sodium thio-sulphate, using starch solution as an indicator.

The number of c.c. thio-sulphate used, subtracted from the 25 c.c. of iodine used, multiplied by the factor 0·96672, and this multiplied by 2 will give the grams of acetone in 100 c.c.

Acetone Oils.

The residue from the dry distillation of crude calcium acetate after separation of the acetone is a dark liquid of extremely complex and variable composition, containing methyl ethyl ketone and other ketones, aldehydes, and various condensation products. It is separated by distillation into two fractions :—

Light Acetone Oil, coming over between 70° and 130°.
Heavy Acetone Oil, coming over between 130° and 270°.

The latter is a non-volatile brown liquid of high viscosity with an unpleasant and persistent odour, sometimes used as a denaturant for alcohol.

Light acetone oil is a pale straw-coloured liquid of low viscosity containing methyl ethyl ketone as the principal constituent. This

is a very powerful solvent of the same class as acetone but strong‹
It differs from acetone in its much slower rate of evaporation a‹
in being insoluble in water, and is used as a solvent for some industr.
purposes. Its value as a solvent is, however, considerably d
counted by the objectionable odour and the wide variations ‹
composition. Different consignments vary both in their physic
data and solvent power so that its use requires continual supervisi‹
and adjustment. The following examples, taken from a large numb
of actual deliveries examined, indicate its physical properties :—

	Sample 1.	Sample 2.	Sample 3.
Colour	Lemon-yellow	Lemon-yellow	Light amber
Reaction	Neutral	—	Neutral
Water content per cent.	—	1·6	3
Specific gravity	0·84	0·876	0·844
Initial boiling point .	70°	71°	65°

Distillation range (%).	Sample 1.	Sample 2.	Sample 3.
70°— 80°	22	} 56	70
80°—100°	32		
100°—120°	24	36	
120°—130°	7	6	} 22
130°—140°	5	2	
Over 140°	10	0	8

Methyl Ethyl Ketone.

Methyl ethyl ketone can be obtained in a state of technical purit
by fractional redistillation of light acetone oil, which yields on tl
average 60 per cent. It is also prepared by distilling a mixture ‹
barium acetate and barium propionate, according to the reaction :-

$$(CH_3)_2 \cdot COOBa + (C_2H_5)_2 \cdot COOBa = CH_3 \cdot CO \cdot C_2H_5 + 2BaCO_3.$$

Like acetone, methyl ethyl ketone is soluble in water. It is rath‹
superior to it in solvent power and has the advantage of having ‹
slower rate of evaporation and a higher flash point. It boils at fro‹
70° to 82°, and has a specific gravity of 0·808 at 20°. A good samp‹
is perfectly clear and practically colourless and should contain n‹
more than 0·01 per cent. of organic acid or 2 per cent. of wate‹
and be entirely free from aldehydes. It should leave no trac‹
of tarry residue on evaporation. It is employed on the continer‹

as a denaturant for alcohol, the similarity of boiling points making separation by fractionation nearly impossible.

At the present time, this solvent is practically unobtainable in this country as the supply from wood distillation on the continent is all absorbed locally.

Methyl Acetone.

This solvent is obtained as a by-product in the preparation of acetic acid, methanol and acetone by the destructive distillation of wood. It is of complex composition, consisting mainly of acetone, methanol and methyl acetate.

The proportions in which these are present vary very considerably in the products turned out by different distilleries, according to the conditions under which the refining of the crude product is conducted. They also vary in the same works from time to time according to the relative demand for the various constituents.

In the fractionation of the crude wood alcohol, market conditions determine how much acetone and methyl acetate are separated out as individual products, how much is left in the refined wood alcohol and how much is left in the residual methyl acetone.

The proportion of methanol may vary from 30 per cent. to 85 per cent.

H. W. Haines [3] gives the following as the average composition :—

Acetone	35 per cent.
Methyl acetate	25 ,, ,,
Methanol and minor ingredients	40 ,, ,,

The methyl acetone produced on the Continent, however, is usually higher in acetone, the average range of composition being as follows :—

Acetone (together with minor ketones)	50—55 per cent.
Methyl acetate (and allied esters)	20—30 ,, ,,
Methanol	20—25 ,, ,,

A typical sample gave the following :—

Acetone	45·05 per cent.
Methyl acetate	21·46 ,, ,,
Methanol	32·09 ,, ,,
Minor constituents	1·40 ,, ,,

Methyl acetone should be practically neutral, the acidity, calculated as acetic acid, not exceeding 20 parts per million. When

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properly prepared the colour is clear water-white and it should
quite anhydrous.

According to the composition the boiling point varies over a ra?
between 50° and 70°.

A good sample will show a distillation range of 90 per ce?
between 50° and 60°, with an end-point not exceeding 70°. ?
specific gravity varies in a similar manner from 0·840 to 0·850.

Methyl acetone is an extremely useful solvent for many purp?
on account of its composite nature. There are many substan?
which are only completely dissolved by the combined action of t?
or more different solvents, in either of which they are only partia?
soluble. Some grades of cellulose nitrate, for example, are m?
readily dissolved by methyl acetone than any of its constituents.

In America, it is largely used as the active constituent of pa?
removers diluted with benzol or white spirit and thickened with w?
or soap in the usual manner in order to retard evaporation.

The proportions of the three principal ingredients is determir?
thus :—

Acetone—Messinger method (page 111).
Methyl acetate (see page 122).
Methanol—Verley and Bölsing method (page 106).

B.E.S.A. [4] specifies three grades of methyl acetone according?
the solvent power for cellulose acetate compared with that of p?
acetone. The method of determination is given as follows :—

" Six grams of cellulose acetate (Air Board Specification D. 6?
to be dissolved in 100 c.c. pure dry acetone. A similar solutior?
to be made using the material under examination as solvent. ?
measured volume of each solution is to be taken and alcohol (Sp?
fication D. 9) is to be run in slowly from a burette. The mix?
vessels are to be kept immersed during this operation in a const?
temperature bath at 25°, and well shaken. The alcohol is to be ad?
until a faint permanent opalescence is obtained in each vessel.

" The ratio between the volumes of alcohol required in the t?
solutions, reckoned as a percentage of that required in the p?
acetone solution, represents the solvent power of the material un?
examination."

The solvent power specified is :—

Grade I : 65, compared with pure acetone 100.
   ,,   II : 50   ,,   ,,   ,,
   ,,   III : 30   ,,   ,,   ,,

B.E.S.A. Specifications for Ketones (see page 140).

	Acetone.	Methyl acetone (Grade I).	Methyl ethyl ketone.
Reference	2 D. 22	D. 2	2 D. 1
Date	November 1920	January 1918	November 1920
Colour.................	Colourless	Not specified	Faint yellow
Specific gravity......	0·796—0·801	,,	0·801—0·815
Refractive index ...	Not specified	,,	1·3790
Distillation range: 95 per cent. between	55° and 60° C.	50° and 70° C.	70° and 81° C.
Residue on evapora- tion	0·01 per cent.	0·01 per cent.	0·01 per cent.
Acidity not above .	0·01 ,,	0·02 ,,	0·01 ,,
Alkalinity not above	0·01 ,,	0·02 ,,	0·01 ,,
Moisture	none	none	none
Permanganate test .	10 minutes	—	—
Ketone content......	97 per cent. (calc. as acetone)	55 per cent. (calc. as acetone)	100 per cent. (calc. as *m-e-ke-*tone)
Solvent power	100	65	—
Freedom from higher ketones ...	—	—	No separation on mixture with water
Solubility in NaCl .	—	—	Not above 1 per cent.

Cyclo-hexanone.

This is a synthetic ketone derived from hexalin by condensation thus :—

Hexalin.   *Cyclo-hexanone.*

It is prepared by treating hexalin with chromic acid. It is very similar to hexalin in its properties but has stronger solvent power.

The physical data of cyclo-hexanone follow closely those of hexalin, the boiling point ranging from 155° to 165° and the specific gravity from 0·930 to 0·950, according to the purity of the sample. The flash point is 64°.

Ether.

Ethers are derived from alcohols by combination of two mole-cules with elimination of water. In ordinary technical work the

name implies the most important member of the group, ethyl ethe which has the composition—

$$\left.\begin{array}{l} C_2H_5 \\ C_2H_5 \end{array}\right\rangle O$$

It is produced by distilling alcohol with strong sulphuric acid, whic combines with the water, allowing two radicles to unite. It wa prepared in this way as far back as the sixteenth century.

It was supposed, before the days of systematic chemistry, tha the ether was derived from the sulphuric acid in this process. Hen the name " sulphuric ether," still sometimes applied to it, whic should be regarded as obsolete.

The sulphuric acid first attacks one molecule of alcohol, formir ethyl hydrogen sulphate, and this reacts with a second molecul forming ether and water and releasing the sulphuric acid fo further action, so that a small quantity of acid is capable of con verting a large quantity of alcohol. In practice, further reaction take place, with the formation of various impurities, which a removed by treatment with alkali, separation with water an redistillation.

Ether is a clear white, extremely limpid liquid, exceeding volatile and inflammable and having a characteristic pleasar odour. It boils at 35" and freezes at −129". The specific gravity 0·7195 at 15".

It is soluble in 11 times its volume of water and the commerci product usually contains a trace of water, which is soluble in tl ether to the extent of 1 part in 35 parts. It also generally contain a residual of unconverted alcohol. The standard of the Briti Pharmacopœia is 92 per cent. purity, the specific gravity of th mixture being 0·735. Ether mixes in all proportions with alcoho chloroform, benzene, petroleum distillates and all other organ solvents and with all mineral and vegetable oils. It dissolves fa and waxes, but resins are only soluble in it to a limited exten Owing to its extreme volatility, ether is not often used as a solve in industrial preparations. In combination with alcohol it forn a good solvent for cellulose. This combination is too volatile fo use in cellulose varnishes but is employed in the manufacture collodion and explosives. Ether is largely employed in the pai laboratory as a solvent for the separation of the pigment and vehic preparatory to analysis. Its extreme volatility combined wi solvent power renders it particularly useful for such purposes, as

enables separation to be obtained quickly and the pigment to be obtained quite dry.

Methylated Ether is an impure form of ether obtained by the dehydration of methylated spirit instead of pure alcohol.

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CHAPTER VI

ESTERS

Of this class of organic compounds, formed by the action of organic acid on an alcohol, whereby the two combine with elimintion of water, the principal members used as solvents are the acetate or acetic esters, of the monohydric alcohols.

These esters are chiefly used as solvents in the preparation cellulose varnishes and lacquers; as a class they are not go solvents for natural resins.

Methyl Acetate.

The first member of the series is derived from methyl alcoh and has the composition $CH_3 \cdot COO \cdot CH_3$. It is prepared by distilli the alcohol over calcium or sodium acetate in presence of sulphur acid. It is produced chiefly as a by-product in wood distillatic together with methanol and acetone, and is either separated out the pure state or marketed as methyl acetone (see page 113), accor ing to the demand.

The following analyses of two samples of methyl acetate may l regarded as typical :—

	A.	B.
Colour	Water-white.	Water-white.
Specific gravity at 15	0·9248	0·9231
Acidity (calculated as acetic acid)	0·024 per cent.	—
Residue on evaporation	negligible	trace
Distillation range :		
53° 55°	60 per cent.	66 per cent.
55° 57°	32 ,,	26 ,,
57° 59°	8 ,,	8 ,,
Content of methyl acetate .. .	85·7	86·3

The principal impurity in commercial samples is methano Methyl acetate has only a faint odour, resembling that of methano to which a small quantity of amyl acetate has been added, th characteristic " pear drop " smell of the latter being only faintl developed. It is used principally in the preparation of aeroplan dope, and large quantities were prepared for this purpose during th war. It is freely soluble in water and liable to decomposition b hydrolysis, acetic acid being set free.

Ethyl Acetate.

This is also known as Acetic Ether and is formed by the actio of acetic acid on alcohol. It is usually prepared by distilling dr

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sodium acetate and alcohol with sulphuric acid, the sodium acetate being placed in a retort and a mixture of alcohol and sulphuric acid run in slowly. The retort is then heated by steam, when the ester distils off. The crude distillate obtained is shaken with alkaline water and the ester decanted off, shaken with a solution of common salt to remove any residual alcohol and dried over carbonate of potash.

It is a colourless liquid with a faint ethereal smell, like an extremely dilute solution of amyl acetate. It is miscible with alcohol, ether and chloroform and moderately soluble in water. Like the alcohol, it is hygroscopic, and the absorbed water reacts with the ester, decomposing it into alcohol and acetic acid.

The commercial product is often very impure, containing anything from 30 to 90 per cent. of ethyl acetate, the balance being alcohol, free acetic acid and water. It is also frequently adulterated with benzol and other cheaper diluents.

An average composition for a commercial product of good quality is :—

Ethyl acetate	85	per cent.
Alcohol	14	,, ,,
Water	1	,, ,,
Acetic acid	0·03	,, ,,

This will show a distillation range of 70°—85° and a specific gravity of 0·893—0·895.

Ethyl acetate is largely used as an ingredient of fruit essences, etc. It is also a moderately strong solvent and dissolves most resins. It is a solvent for cellulose nitrate, but on account of its hygroscopic nature it is not of much value for the preparation of cellulose lacquers for metal, as the acetic acid set free by the action of the water attacks the metal, causing discoloration.

If used as a solvent for lacquers it is also liable to cause " blushing " owing to its rapid evaporation. It is claimed, however, that this defect is entirely due to the impurities in the ethyl acetate. A pure anhydrous compound is produced in America and also in Germany which is claimed to be very much more satisfactory as a solvent. This has a boiling point of 78°.

The solvent known as " ansol " is a mixture of absolute alcohol and anhydrous ethyl acetate which is claimed to be capable of dissolving all resins and to be free from the tendency to cause " blushing " in cellulose varnishes and lacquers.[1] It is somewhat difficult to understand how the anhydrous condition is maintained

in such a mixture, considering the hygroscopic nature of both ingredients.

Butyl Acetate.

This solvent is of comparatively recent introduction and closely similar in its properties and reactions to amyl acetate; the odour of the two is practically identical and owing to its lower price butyl acetate is sometimes supplied for amyl acetate. It is prepared by distilling butanol over calcium acetate in presence of sulphuric acid, whereby the alcohol is converted into the ester by the nascent acetic acid formed. It is also prepared by the direct action of glacial acetic acid on the alcohol, generally in presence of a small quantity of phosphoric acid. The physical data are :—

Colour	water-white.
Specific gravity	0·870 to 0·873 at 16°.
Acidity	not exceeding 0·03 per cent. calculated as acetic acid.

The commercial article averages 85 per cent. of butyl acetate. It is anhydrous, a good sample mixing in all proportions with benzene without clouding.

A typical sample gave the following distillation range : —

Below 107	none.
107° 120	40 per cent.
120° 135	55 ,, ,,
Residue	5 ,, ,,

Unlike the esters of the lower alcohols, butyl acetate is only slightly soluble in water (0·9 volume is dissolved in 100 volumes of water).

Butyl acetate is a powerful solvent and one of the best for all types of cellulose, including cellulose nitrate, cellulose acetate and celluloid. It is an excellent solvent for the purpose, as it is intermediate in rate of evaporation between ethyl and amyl acetates. Its rate of evaporation is sufficiently slow to permit the film to flow smoothly and allow for the evaporation of moisture. It therefore gives a clear smooth film without any tendency to " blushing." Being non-hygroscopic, it is quite stable in solution and does not tend to develop an acid reaction. The enormous expansion of the use of cellulose lacquers has largely been rendered possible by the introduction of butyl acetate on a commercial scale; before its

advent the production of this type of lacquer was dependent on the supply of amyl acetate, which was itself dependent on fusel oil; the supply of this is limited and uncertain, whilst the composition is extremely variable.

Butyl acetate of uniform composition approximating to 98 per cent. purity is available in quantities only limited by the supply of the butanol from which it is prepared, and has largely supplanted amyl acetate. It is estimated that over three-quarters of the total production of butanol is converted into acetate at the present time. It is also used as a solvent for synthetic resins. The solvent power of the esters for synthetic resins of the phenol–formaldehyde type decreases with the complexity of the molecule. Thus butyl acetate is a better solvent than amyl acetate, but not so powerful as ethyl acetate.

Amyl Acetate.

This was introduced as a solvent in 1882, when J. N. Stevens took out a patent for its use for the preparation of cellulose nitrate solutions. It is prepared from fusel oil, the usual method being to mix 100 parts of anhydrous sodium acetate, 100 parts of commercial amyl alcohol and 130 parts of concentrated sulphuric acid, allow the mixture to stand for about 12 hours for the reaction to take place, and then distil. It is purified by shaking with water to remove soluble impurities and re-distilled.

Theoretically, eight isomeric forms are possible and the properties of the acetate vary according to which of these alcohols is used. The commercial preparation is usually derived from iso-amyl alcohol.

On account of the variation in the raw material (see amyl alcohol) the composition of amyl acetate is not very uniform and it is often far from pure. It is a colourless liquid with a characteristic and very penetrating ethereal odour resembling pineapple, which is pleasant in small concentration but becomes quite overpowering if one is exposed to strong concentration of the vapour for a long period. It is not highly inflammable, the flash point being 77° F.

Amyl alcohol in the acetate can be separated and determined by shaking the sample in a graduated tube with a mixture of equal volumes of glacial acetic acid and water. This dissolves amyl alcohols but not the acetate.

Amyl acetate differs principally from the butyl ester in having a higher boiling point, 148°, and in evaporating more slowly.* For

* The specific gravity is very close to that of butyl acetate, averaging 0·875.

most technical purposes the two are equivalent, apart from variatio in strength and purity, which are more marked with the amyl th with the butyl ester. It is employed in the same way as bu acetate, as a solvent for cellulose and also as an odoriser, added small quantities to fruit essences, etc., to impart its characteris smell.

B.E.S.A. Specifications for Acetic Esters (see page 140).

	Methyl acetate.	Ethyl acetate.	Butyl acetate.	Amyl acetate.
Reference	D. 13	D. 19	2 D. 4	2 D. 3
Date	Dec. 1917	May 1918	November 1920	November 19
Colour	Colourless	Colourless	Colourless	Colourless
Specific gravity ...	0·920 0·942	0·890 - 0·905	0·875 - 0·880	0·870—0·87
Distillation range, 95 per cent. between	55° and 68°	70° and 80°	110° and 130°	125° and 14
Residue on evaporation, not above .	0·01 per cent.	0·01 per cent.	0·01 per cent.	0·01 per cer
Acidity, calculated as acetic acid, not above	0·1 ,,	0·1 ,,	0·01 ,,	0·01 ,,
Moisture	none	none	none	none
Ester content not less than	80 per cent.	90 per cent.	87·5 per cent.	90 per cent
Solvent power (see page 114)........	76	Not specified	Not specified	Not specific

The ester content is determined by the following method :—

About 1 gm. of the material is weighed into a small tared tu and the tube and its contents are immediately transferred to flask containing 25 c.c. of approximately $N/2$-alcoholic caustic so solution. A water-cooled reflux is fitted to the flask, and the latt heated for one hour on a water-bath at 100°, at the end of whi period the condenser is rinsed with neutral distilled water. Aft cooling, the flask is removed, and the contents are titrated wi $N/2$-hydrochloric acid, using phenolphthalein as indicator.

A blank determination is made on the alcoholic caustic so under similar conditions.

One c.c. of $N/2$ acid is equivalent to 0·037 methyl acetate.
,, ,, ,, ,, 0·044 ethyl acetate
,, ,, ,, ,, 0·058 butyl acetate
,, ,, ,, ,, 0·065 amyl acetate.

Hexalin Acetate.

Hexalin (page 105) can be esterised by treatment with organic acids in the same way as the alcohols of the fatty hydrocarbons, and hexalin acetate has been used in Germany as an alternative to amyl acetate when the supply of the latter failed. It has great possibilities as a solvent, as it has a greater solvent power for cellulose nitrates and acetates than amyl acetate and dissolves freely both natural and synthetic resins. It is a liquid of a slight straw colour, with a higher boiling point and a slower rate of evaporation than amyl acetate. Unfortunately, it has an extremely penetrating and persistent smell, which is unpleasant even in low concentrations, having a peculiar " bad fruit " quality quite unlike the pineapple flavour of the esters previously described. Prolonged exposure to the vapour, even in low concentration, has a distressingly irritating effect and causes persistent headache. Opinions differ, but in the present writer's opinion it can scarcely be regarded as a suitable solvent for industrial preparations, except in very small proportion, on this account. The physical properties are :—

Boiling point	165°—180°
Specific gravity at 20°	0·965—0·970
Refractive index	1·438—1·439
Flash point	64°

Ethyl Carbonate.

The ethyl ester of carbonic acid, having the composition :—

$$\begin{matrix} C_2H_5 \cdot O \\ \\ C_2H_5 \cdot O \end{matrix} \Big> C = O,$$

has been known in the laboratory for many years, but has only been produced on an industrial scale quite recently. It was originally made by treatment of silver carbonate with ethyl iodide and is prepared on the large scale by synthesis from alcohol.

It is closely similar to ethyl acetate in its properties and decomposes in presence of water in the same way. As this decomposition results in the liberation of carbonic instead of acetic acid, it has the advantage over ethyl acetate of not being liable to react with metals, and it can be used as a solvent for metal lacquers, as it is an excellent solvent for both cellulose and resins. It has a boiling point of 126° and only a faint ethereal odour similar to that of the acetate.

Ethyl Lactate.

This is prepared by the action of commercial lactic acid, obtaine by the fermentation of waste sugar, distillery-wash, etc., on alcoho It has the composition :—

$$CH_3 \cdot CH \cdot OH \cdot COO \cdot C_2H_5 \text{ (ethyl ester of hydroxypropionic acid).}$$

It is a mobile liquid with a very slight colour and a peculia ethereal smell which causes a mild tingling effect on the nose. Th physical properties, according to H. A. Gardner [3] are :—

Specific gravity	.	.	.	1·0385
Initial boiling point	.	.	.	125°
Distillation range	.	.	.	98 per cent. 144° to 159°
Flash point	.	.	.	117° F.

It has therefore a higher boiling point than any of the acet esters. On this account it has been recently introduced as a slov drying solvent in the preparation of cellulose varnishes. Gardne finds that it produces a relatively more viscous solution than buty acetate and that the solution is more stable, standing dilution wit three times as much benzol as the butyl acetate solution befor separation takes place.

Experience varies as to its value as a solvent; B. R. Tunison considers that it is one of the most useful solvents for cellulo obtainable. Other experimenters, however, have experienced diff culty with its use and find that it has a pronounced tendency t cause " orange-peel effect " and rapidly hydrolyses in presence o moisture.

Probably the suggestion made by Gardner is correct, that i should be used in relatively small amounts in combination wit other solvents.

Butyl Propionate.

This is a high-boiling liquid, distilling between 140° and 145° which is used when a higher-boiling solvent than amyl acetate i required.

Formic Esters.

These are produced by the esterification of alcohols with formi acid in the same way as the acetates are produced with acetic acid The series of esters thus formed are closely similar to the correspond

ing acetic esters in their properties. The following are used to a limited extent as solvents :—

	Boiling point.	Specific gravity.
Methyl formate	32°	0·974
Ethyl formate	54°	0·925
Butyl formate	98°	0·885
Amyl formate	116°	0·881

Specifications were drawn up by the British Engineering Standards Association during the war,[2] but the materials are now rarely called for.

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CHLORINE DERIVATIVES

By the substitution of hydrogen by chlorine in various membe
of the paraffin and olefine series of hydrocarbons a number of usel
solvents are obtained which form a group having the same gene
characteristics. These differ in the following respects from those
all the other groups of solvents previously considered, the differen
being mainly due to the content of chlorine.

1. High specific gravity, heavier than water.

2. Low inflammability; in most cases completely no
inflammable.

3. Low heat of vaporisation, resulting in extreme volatility.

4. Pronounced anæsthetic properties and in some cases dangere
toxic effects.

5. Liability to decomposition with formation of hydrochlo
acid.

The first three of these distinctive properties, combined with t
fact of their high solvent power for a very wide range of orgar
substances, render this group of great value for many industr
purposes. It is unfortunate that their usefulness is discount
for many purposes by the pronounced toxicity. Were it not
this they would undoubtedly take the first rank as industr
solvents, particularly on account of the freedom from fire ris
A non-inflammable, non-poisonous solvent would obviously be
immense industrial value and the demand for it is constant a
insistent. Unfortunately, no substance has yet been produc
which combines these three properties of high solvent power, no
inflammability and absence of toxicity.

Methylene Chloride.

This is methane or marsh gas, CH_4, in which two atoms
hydrogen in the molecule have been replaced by chlorine, giv
the composition CH_2Cl_2.

It has a boiling point of 42° and a specific gravity of $1\cdot32$.

It is a water-white liquid resembling chloroform in gene
properties, which is claimed to be absolutely non-inflammal
This is not strictly correct, however, although it is less inflamma
than dichlorethylene. A technical product which avera
98 per cent. purity has been recently produced on an indust
scale and introduced for use where a non-inflammable solvent
low boiling point is required. It can be used, for instance, in pl
of solvent naphtha, as it is a strong solvent for oils and resins, a

also for raw rubber. It evaporates very rapidly at a low temperature and leaves no trace of residue.

It is a solvent for cellulose and can be used with advantage in certain types of nitrocellulose varnishes to increase the flowing qualities and lower the flash point. It is not, however, suitable for the preparation of varnishes and lacquers for metal work, owing to its tendency to decomposition with formation of hydrochloric acid.

Chloroform.

This is derived from methane, CH_4, by substitution of three of the four hydrogen atoms by chlorine, the formula being $CHCl_3$. It is prepared in several different ways, the original method discovered in 1831 being to distil chloral hydrate with sodium hydroxide.

By this process the chloroform is obtained in a state of absolute purity, but it is comparatively costly.

Commercial chloroform can be obtained by the action of chlorine or bleaching powder on wood alcohol or alcohol. This is effected by digesting a mixture of alcohol and bleaching powder solution in definite proportions at about 60°, and then distilling off the resulting product.

At the present time, the bulk of the chloroform produced is obtained from crude acetone. The acetone is diluted with water and gradually added to a solution of bleaching powder, when the chlorination takes place in the cold. Trichloracetone is first formed, which is then attacked by the calcium hydroxide set free, with the production of calcium acetate and chloroform, the reactions being :—

$$2(CH_3 \cdot CO \cdot CH_3) + 3Ca(OCl)_2 = 2(CH_3 \cdot CO \cdot CCl_3) + 3Ca(OH)_2$$
$$2(CH_3 \cdot CO \cdot CCl_3) + Ca(OH)_2 = Ca(CH_3 \cdot COO)_2 + CHCl_3.$$

Various other methods of preparation have formed the subject of patents,[1] but they are not employed industrially to any large extent.

Chloroform is a water-white liquid of characteristic ethereal odour. The specific gravity is 1·48 at 15° and the boiling point 61°. It solidifies on cooling to —70°. The refractive index is 1·449. The vapour density, according to Livache, is 4·19.

Its most important use is as an anæsthetic, but it is also used largely as a solvent. It is the most effective solvent, for instance, for extracting the free sulphur from pigments such as ultramarine and cadmium sulphide, where very pure sulphur-free grades are required for special purposes such as artists' use.

It is also a solvent for rubber and gutta percha and most resi
Only the hardest resins such as amber resist complete solution
prolonged shaking with chloroform. It is only soluble to the ext
of 1 part in 200 parts of water, but mixes in all proportions w
all organic solvents and vegetable and mineral oils. Exposed
any length of time to the light in presence of moisture, chlorofo
is liable to decomposition with formation of hydrochloric ac
For medicinal work, therefore, it is important that it should
freshly distilled. The addition of a small quantity of absolt
alcohol prevents this decomposition. It is extremely volatile a
lowers the temperature to such an extent by its rapid evaporati
as to cause freezing. It is practically non-inflammable, but can
ignited with difficulty.

Carbon Tetrachloride.

This substance consists entirely of carbon and chlorine, t
formula being CCl_4. It may therefore be regarded as the fii
stage in the chlorination of methane, or chloroform in which t
last remaining atom of hydrogen has been replaced by chlorine.

It is generally prepared from carbon bisulphide, either by passi
a mixture of chlorine and carbon bisulphide vapour through a r
hot porcelain tube or by passing chlorine through the liquid
sulphide in which a little iodine has been dissolved to act as
catalyst. In the latter case sulphur chloride is formed as a b
product and the carbon tetrachloride is separated from it by d
tillation and purified in the same way as chloroform. A lat
patented process starts with a mixture of sulphur chloride a
carbon bisulphide which is heated in presence of a metallic cataly
preferably iron, when carbon tetrachloride and sulphur are produc
according to the reaction :—

$$CS_2 + 2S_2Cl_2 = CCl_4 + 6S.$$

These reactions form the basis of the continuous process of Cot
in which the vapours of chlorine and carbon bisulphide pass over
catalyst consisting of asbestos impregnated with manganese chloric
The mixture of sulphur chloride and carbon tetrachloride produc
is mixed with more carbon bisulphide and heated in contact wi
metallic iron. The sulphur chloride is then decomposed with t
formation of more carbon tetrachloride which distils off, and fi
sulphur which melts and runs back to an electric furnace, where
is reconverted to carbon bisulphide and returned to be treated wi
fresh chlorine.

Carbon tetrachloride closely resembles chloroform in appearance, odour, and general properties. It is distinguished from it by the higher specific gravity, 1·629, and boiling point, 77°, and by being quite non-inflammable. On this account it is largely used for " dry cleaning " of fabrics and as an extraction agent. At one time it was used as a " dry shampoo " in hair-dressing establishments, oblivious of its physiological action, which is similar to that of chloroform, but fatalities led to the discontinuance of this practice.

Carbon tetrachloride is a solvent of the same order as chloroform. It mixes with other organic solvents, is only soluble in water to a slight extent and dissolves vegetable and mineral oils. It dissolves most of the resins in the cold, but the hard fossil copals only dissolve with difficulty. In common with all the chlorinated compounds, it is not a good solvent for shellac. A mixture of equal parts carbon tetrachloride and alcohol will, however, dissolve shellac to the extent of about 25 per cent.

It is used to some extent as a solvent in the rubber industry, especially to replace naphtha and petroleum spirit in the preparation of rubber solutions which have to be transported any distance, in order to obviate the fire risk.

In contact with water it slowly decomposes with formation of hydrochloric acid :—

$$CCl_4 + 2H_2O = 4HCl + CO_2,$$

on this account it rapidly corrodes iron vessels in presence of moisture, which is a great drawback to its industrial use. It is essential to use either non-metallic containers or lead- or tinned-lined vessels for its storage.

Chlorides of Ethane and Ethylene.

Tetrachlorethane	Dichlorethylene
Pentachlorethane	Trichlorethylene
	Perchlorethylene

The use of these products on an industrial scale dates from about the year 1906, when their manufacture was introduced in Germany by the Consortium für Elektrochemische Industrie of Nuremberg. They were introduced into this country by R. W. Greeff, and about 1908 Gustav Koller came over from Germany and started their manufacture for the Weston Chemical Co. of Runcorn.

The first published account of their production and uses in this country is given in a paper by Koller.[3]

9

The starting point in the production of this series is acetyle which is combined with chlorine direct to form tetrachloreth according to the reaction :

$$C_2H_2 + 2Cl_2 = C_2H_2Cl_4.$$

Under ordinary conditions these two gases combine w explosive violence on mixing, but by careful regulation of the c ditions as regards temperature and pressure, etc., it is possible arrange so that the reaction takes place slowly. The success of production on an industrial scale depends on the control of reaction in this manner.

Tetrachlorethane is converted into Trichlorethylene on tre ment with slaked lime, according to the reaction :

$$2(C_2H_2Cl_4) + Ca(OH)_2 = 2C_2HCl_3 + CaCl_2 + 2H_2O.$$

From trichlorethylene, Perchlorethane is produced by furth chlorination, the reaction being effected by exposure to chlor gas in presence of a catalyst, according to the equation :

$$C_2HCl_3 + Cl_2 = C_2HCl_5.$$

This again on treatment with lime yields Perchlorethylene :

$$2C_2HCl_5 + Ca(OH)_2 = 2C_2Cl_4 + CaCl_2 + 2H_2O$$

On further treatment with chlorine in presence of a catalyst t can be finally converted into Hexachlorethane, C_2Cl_6, which i solid product used as a non-inflammable plasticiser for cellulose.

Dichlorethylene. The commercial product is not a pure substan but a mixture of two isomeric compounds with the compositi $C_2H_2Cl_2$ in the proportion of approximately three-fifths of a co pound boiling at 60 and two-fifths of one having a boiling point 48 . The boiling point of the mixture, therefore, ranges betwe these two extremes, averaging 52 . The mean specific gravity 1·278 at 15 .

It is a powerful solvent and its usefulness lies in its low boili point and rapid volatility, combined with low inflammabili For some purposes, such as the extraction of some dyes, perfumes a other organic substances, which are only stable at temperatu below the boiling point of water, a solvent of very low boiling po is essential. Such solvents in general give off a dangerously flammable vapour on evaporation, which is a serious drawback operations on an industrial scale.

Dichlorethylene is insoluble in water but mixes with alcol freely. A mixture of industrial spirit and dichlorethylene forms useful solvent for resins such as shellac, which is considerably l

inflammable than the pure spirit. It is not correct, however, to say that dichlorethylene is entirely non-inflammable. Above 36° F. it gives off a vapour which can be ignited, but the combustion absorbs heat and consequently cools the vapour so that the flame extinguishes itself, and it is not inflammable from the point of view of fire risk.

It is a water-white liquid, with a smell resembling chloroform— which is characteristic of all the series—and anæsthetic in property. Although the vapour produces insensibility if breathed, this rapidly passes off on exposure to fresh air and no serious toxic effects result. It is a strong solvent for most organic substances and in particular dissolves rubber very readily. It is a fairly stable compound, but is gradually decomposed on exposure to light in presence of moisture, liberating hydrochloric acid. On boiling with strong alkali it is decomposed with formation of mono-chlorethylene, which is an unstable explosive substance.

Trichlorethylene, technically known as " Westrosol," is closely similar to dichlorethylene in appearance and smell, but has a higher boiling point and specific gravity.

It is a definite chemical compound having the constitution :—

$$CHCl - CCl_2.$$

Unlike dichlorethylene, therefore, it has a constant boiling point and the commercial product should distil completely within 1° of 87°. The specific gravity is 1·47, so that it is considerably heavier than water and may be kept under water to prevent evaporation. In its chemical reactions it is identical with dichlorethylene. It is essential to store it away from exposure to sunlight and small quantities in the laboratory should not be exposed in plain bottles, but kept either in amber bottles or metal containers, as it decomposes in the light, developing hydrochloric acid and phosgene.

It is claimed that it does not attack ordinary metals like iron and steel, but this is only true so long as it is pure, which can only be ensured if it is kept sealed from the light and anhydrous. On account of this liability to decomposition in presence of light it is not advisable to use any of these ethylene derivatives for treatment of any material which is readily attacked by acids.

This solvent is chiefly used as an agent for the extraction of oil from seeds; owing to its extremely low latent heat it evaporates very rapidly and being a pure substance leaves no " tail " or residue.

On account of its non-inflammability it is used largely for the " dry cleaning " of fabrics and the degreasing of textiles, etc.

Trichlorethylene has been employed in Germany as a solven
in the extraction process of preparing wood turpentine. It i
an extremely powerful solvent, dissolving all oils, most resin:
rubber and many inorganic substances such as sulphur an
phosphorus and is particularly efficient because of its great pene
trative power. It does not dissolve cellulose nitrate or acetate b
itself, but in combination with phenol and particularly the hydro
genated phenols such as hexalin it readily acts as a solvent fo
these substances. On account of its solvent power it is used as
cleaning agent, and in combination with soft soap (with which i
forms a stable emulsion miscible with water) it is used in the prepara
tion of solvent soaps. Like all the chlorinated solvents, its vapou
is anæsthetic, and prolonged exposure produces fainting, but as wit
dichlorethylene the effect is transient and no serious after-effect
are produced.

Perchlorethylene.—has the same relation to ethylene as carbo
tetrachloride has to methane, being completely chlorinated an
having the constitution :—

$$CCl_2 = CCl_2.$$

Its specific gravity is very high, 1·624 at 15°, and it has a constan
boiling point of 119°. With the exception of this difference i
physical constants its properties are identical with those of tri
chlorethylene. It is used where a solvent with a slower rate c
evaporation is required.

Tetrachlorethane is the best known of this series of solvents an
is technically known as " Westron." It has the constitution :—

$$CHCl_2 - CHCl_2.$$

It is a water-white liquid with an odour closely resembling that c
trichlorethylene and is similar to the ethylene derivatives in many c
its properties, although differing from them in some importan
respects. It is considerably heavier than trichlorethylene, having
specific gravity of 1·601 at 15°. It is, in fact, the heaviest solvent c
industrial importance. The boiling point is high, 147° at norma
pressure (144° at the reduced pressure of 738 mm.). Owing to it
low specific heat and latent heat of evaporation, its rate of evapora
tion is extremely rapid, in spite of the high boiling point. Th
vapour is entirely free from danger as regards fire risk, as it i
perfectly non-inflammable.

Chemically it is more stable than trichlorethylene and not s
readily decomposed by light, although it is advisable not to store i

in clear glass bottles.   It is, however, decomposed in presence of
moisture and will consequently corrode iron unless care is taken to
ensure that it is quite anhydrous.   It should be stored in lead- or tin-
lined containers to ensure freedom from reaction.

It is decomposed by alkalies with formation of trichlorethylene
and alkali chloride and cannot therefore be used for the preparation
of solvent soft soaps in the same way as trichlorethylene.

Its physiological action is much more pronounced than that of
the ethylene derivatives.   In addition to the vapour having a
pronounced anæsthetic effect, prolonged exposure to the fumes
causes specific illness, as it attacks the liver.   It is essential that it
should not be used to any extent in confined spaces, and unless care
is taken to provide ample ventilation serious and even fatal illness
may be caused.   It should be noted that on account of its high
specific gravity the vapour is considerably heavier than air, and the
ventilation of workshops in which it is used should accordingly be
downwards and not upwards.   If care is taken to provide adequate
ventilation, carrying off the vapour in this way so that no great
concentration can exist at the level at which the air is inhaled by
workers, it can be used freely without danger.

Tetrachlorethane is the most powerful solvent of this group.
It is insoluble in water but it mixes freely with alcohol and all organic
solvents.   It is a good solvent for all oils, fats and waxes and dissolves
soft resins completely.   It also attacks hard resins but does not
dissolve them completely in the cold in the same way as the higher
alcohols.   It also attacks oxidised oils and forms a very efficient and
rapid paint and varnish remover.   For this purpose it is an advantage
to dissolve in it a substance such as stearine which remains incor-
porated with the softened film and prevents it from hardening off on
the rapid evaporation of the solvent.

Tetrachlorethane is also a good solvent for pitches and bitu-
minous substances.   On account of its solvent power for resins
combined with its rapid rate of evaporation it forms a useful thinner
for paints for special purposes required to dry rapidly and give a
hard and fairly tough film.   Apart from the unpleasant effect of its
vapour, it is too powerful a solvent for ordinary paints except for
application by spraying, as the undercoat would be moved on the
application of a second coat by the brush.

Unlike trichlorethylene, it is also a solvent for cellulose nitrate
and cellulose acetate and may be used for the preparation of non-
inflammable cellulose varnishes.   It is a solvent for many inorganic
substances, notably sulphur and phosphorus.   It dissolves only 1 per

... of sulphur at ordinary temperatures, but the solubility increase rapidly as the temperature rises and at 120° it mixes in all propo tions. This property is utilised for the extraction of free sulphu from compounds, the operation being conducted at a fairly hig temperature and the sulphur crystallised out of the tetrachlorethan on cooling.

It is largely used for extraction purposes in the same way a trichlorethylene, and for the degreasing of metals, etc. Owing t its toxic properties it is also extensively employed as an insecticide but its toxicity to human beings as well as to insects militates agains its use for this purpose except for spraying fruit trees and othe open-air work.

Owing to its non-inflammable nature and the heaviness and penetrating power of the vapour it is found quite effective as a fir extinguisher.

Pentachlorethane is a solvent closely resembling tetrachlorethan but is distinguished from it by its high boiling point, 159°, and slower rate of evaporation. It has the highes specific gravity of all the volatile solvents, 1·685 at 15°. It is onl occasionally used as an industrial solvent.

The following table, published by the Weston Chemical Co., give some of the physical properties of this group of solvents :—

			Perchlor ethylene.	Sym tetra chlor ethane.	Penta chlor ethane.	Hexa- chlor- ethane.
			C_2Cl_4	$C_2H_2Cl_4$	C_2HCl_5	C_2Cl_6
			166·8	167·8	202·3	236·7
			119°	144°	159°	185° subl
			14 mm.	11 mm.	7 mm.	3 mm.
			0·273	0·246	0·268	0·266
			50·59 Cal.	51·39 Cal.	54·43 Cal.	43·64 Cal.
			0·001183	0·001078	0·000908	0·000909
			23	19	36	·22
		1·278	1·171	1·624	1·6011	1·685	2·09

Chlorbenzenes.

Two of the several possible chlorine derivatives of benzene are prepared on an industrial scale for use as solvents, namely :—

	Boiling point.	Sp. gr.	Flash point.
Monochlorbenzene .	132°	1·11	?
Dichlorbenzene ...	172°	1·35	62°

The latter is a mixture of the ortho and para varieties in the approximate proportion of 75 and 25 per cent. respectively. Mono-chlorbenzene is prepared by the direct action of chlorine on benzene in presence of iron as a catalyst, the crude product being purified by fractionation in vacuo. Both these substances dissolve soft resins, but damar is soluble only in mono-chlorbenzene. Copals and other hard resins are insoluble in either.

They are used to some extent as solvents, but are rather difficult to work with. Dichlorbenzene is not a good practical solvent for spirit varnishes, etc., as it does not give a good film on drying. The mono-chlorbenzene, however, gives a film which dries with a matt surface and is useful for preparing dull finishes.[5] Like all chlorine derivatives, these solvents are decidedly toxic in their properties, but their toxic effect on human beings is not nearly so pronounced as that of the chlorinated petroleum hydrocarbons. Dichlorbenzene has been used in place of tetrachlorethane on that account as an insecticide and for the preservation of timber against attack by insects. The following composition was used in the preservation of Westminster Hall :—

op-Dichlorbenzene	.	.	.	.	.	91 per cent.
Castile soap	.	.	.	.	.	7 ,, ,,
Cedar wood oil .	.	.	.	.	.	2 ,, ,,

Dichlorhydrin.

When glycerol is treated with hydrochloric acid, one or more of the hydroxyl groups can be substituted by chlorine to form one of the five possible compounds known as Chlorhydrin.

Commercial chlorhydrin is the α-dichlorhydrin, in which the two outer members are chlorinated thus :—

$CH_2 \cdot OH$	$CH_2 \cdot Cl$
$CH \cdot OH$	$CH \cdot OH$
$CH_2 \cdot OH$	$CH_2 \cdot Cl$
Glycerol.	*Dichlorhydrin.*

This solvent is prepared by mixing glycerol with fifteen times it weight of concentrated hydrochloric acid and heating the mixtur to 100 for some hours. The mixture is then extracted with ether an the ethereal solution is distilled. After the ether has all been drive off the temperature rises and a distillate is collected up to 230 This is treated with lime, again extracted with ether, and th chlorhydrin finally obtained by evaporation of the ether. Anothe method is to heat anhydrous glycerol with a solution of sulphu chloride in sodium chloride for several hours. Dichlorhydrin is colourless syrupy liquid with a rather pleasant smell, moderatel soluble in water (1 volume requiring 10 volumes of water) an readily in alcohol and ether. The boiling point is 178 and th specific gravity 1·37. It can be converted into mono-chlorhydri by treatment with caustic potash in the cold and further chlorinate to epichlorhydrin by prolonged digestion with hydrochloric acid.

Dichlorhydrin is a moderately strong solvent for resins. The sof resins such as Elemi, Damar, Mastic and Manilla dissolve fairl readily, but on warming or keeping for any length of time th solutions lose colour, turning a deep brown. The fossil copa such as Zanzibar and Sierra Leone are only partially soluble eve on heating, and the solution turns brown in the same way. Kaur i, however, almost completely soluble. Dichlorhydrin is a goo solvent for shellac, both natural and bleached. With the latter i readily effect complete solution, giving a pale coloured solutio which does not discolour Like most chlorine derivatives it is no readily inflammable, and is liable to decomposition in presence o water with formation of hydrochloric acid.

Epichlorhydrin.

This is formed by the removal of one molecule of hydrochlori acid from dichlorhydrin thus :

$$
\begin{array}{ll}
\begin{array}{l}
CH_2Cl \\
CH \cdot OH \\
CH_2Cl
\end{array}
&
\begin{array}{l}
CH_2Cl \\
CH \\
CH_2
\end{array} \Big) O
\end{array}
$$

Dichlorhydrin.   *Epichlorhydrin.*

It is prepared by saturating a mixture of glycerol and glacial aceti acid with hydrogen chloride and distilling the mixture, collectin the distillate between 180 and 220°. This distillate is then treate with caustic potash and fractionated.

Epichlorhydrin is a liquid resembling chloroform in appearanc and colour. It has a boiling point of 117° and sp. gr. 1·194.

differs considerably in its solvent action from dichlorhydrin. The soft resins are freely soluble in the cold, giving solutions which do not discolour. Hard copals are partially soluble in the cold and freely soluble on heating, giving very pale solutions which do not discolour and form hard brilliant films on drying. Manilla and Kauri are, however, not so readily soluble as in dichlorhydrin, whilst bleached shellac is practically insoluble.

These chlorhydrins are not used extensively for industrial purposes, but are employed in the preparation of special varnishes such as photographers retouching varnish.

A chlorinated ester—β chlorethyl acetate—has been proposed as a solvent for cellulose acetate and nitrate.[6]

CHAPTER VIII.

SULPHUR DERIVATIVES CARBON BISULPHIDE

THE only volatile solvent in industrial use which contains sulph
is carbon bisulphide, which therefore requires a brief chapter
itself.

Technical literature is about equally divided in the use of t
name carbon bisulphide and carbon disulphide for this substanc
The former has been adopted in this work as the most rationale.

The composition is indicated by the formula CS_2. It was d
covered in 1796 by Lampadius, who prepared it by the direct unic
of sulphur and carbon at a low red heat. On the industrial sca
this reaction is carried out in a cylindrical cast-iron retort fitt
with a porcelain tube which reaches almost to the bottom. T
crude distillate is washed by scrubbing with lime to remove hydroge
sulphide (contained as a by-product derived from hydrogen occlude
in the charcoal) and then distilled in a water jacketed still
presence of small quantities of fatty oil, water and lead acetate
remove other impurities. In order to obtain it perfectly pure it
necessary to remove the last traces of by-products by prolonge
shaking with a small percentage of mercuric chloride, which combin
with the evil smelling poly sulphides to form an insoluble compoun
The sludge thus formed is removed by decantation and the liqu
re-distilled over the water bath.

This process has now been largely superseded by the electr
furnace process due to Taylor.[7] This furnace is constructed of tv
concentric brick cylinders, fitted at the base with two carbo
electrodes. Carbon and sulphur are fed into the furnace in separa
continuous streams, when the sulphur is vaporised by the heat fro
the electrodes and rises through the furnace to meet the stream
carbon, with which it reacts to form the carbon bisulphide. Th
is led into the condenser as it forms and purified as described above

The pure carbon bisulphide obtained in this way is perfect
clear and water white, and has a smell resembling that of chloroforr
only much more pungent. The ordinary commercial article, hov
ever, is pale yellow in colour, with a penetrating evil odour, due t
the presence of a small quantity of other organic sulphur derivative
The specific gravity is 1·268 for the pure article, but rises to 1·29
in ordinary commercial samples. It boils at 46°.

In contra distinction to the chlorinated solvents, carbe
bisulphide is highly inflammable, the flash point being −20°, and it
liable to spontaneous ignition on exposure to the air at a temperatu
approximating to the boiling point of water, whilst the vapour forn

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an explosive mixture with air at ordinary atmospheric temperatures. From the point of view of fire risk, therefore, it is about the most dangerous solvent used in commerce.

The inflammability, combined with decided toxic action, limits its industrial uses, which is unfortunate, because as a solvent it is extremely useful. It dissolves readily, not only all oils, fats and waxes, most of the resins, and organic substances such as camphor, tar, rubber and guttapercha, but also many inorganic substances, including sulphur, phosphorus and iodine.

It is decidedly the most effective solvent for rubber known, and was at one time largely used in the rubber industry, particularly as a thinner for sulphur chloride in the cold cure process of vulcanisation. Owing to its rapid penetration of the rubber it brought the sulphur chloride dissolved in it quickly into contact with every portion of the article to be vulcanised and rendered the process of curing more rapid and uniform. Its use for this purpose has, however, been largely abandoned, owing to the restrictions placed on its transport and use on account of its dangerous inflammability and toxicity. It is used to a considerable extent as an extraction agent and for various special purposes. It forms a very effective insecticide and is used for dressing vines and other plants infested with insect pests.

Dr. Alexander Scott [8] recommends the use of carbon bisulphide vapour as the most effective for killing boring insects in wood. It proves rapidly fatal to the insects, and careful experiment has revealed no deleterious action on the painted surface in the case of treatment of painted panels so infected.

It is miscible in all proportions with most organic solvents, but is only soluble in water to the extent of 1 per cent. Like most sulphur compounds, it has a very high refractive index (1·601) and its optical properties are particularly useful in physical work, because it combines with this high refractive power an exceptionally high dispersive power.

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If the difference is below 150 mm. the colour is graded accord
to the scale :

Water white	.	.	.	.	.	.	150 mm. or mo
Standard	.	.	.	.	.	.	50 to 150 mn
One shade off	.	.	.	.	.	.	25 50 mm.
Two shades off	.	.	.	.	.	.	15 25 mm.[5]

The I.P.T. method is the more accurate of the two, as it provie
for the well known fact that the absolute colour varies with t
concentration, as will be seen from the colour analyses given abo
For this reason a special scale should be constructed for each solve
for accurate work, although the petroleum scale can be applied
other solvents with sufficient accuracy for most industrial purposes.

Specific Gravity   The figures given for the specific gravities
solvent as published works are often very conflicting.   Examinati
shows that this is largely due to the fact that the observations ha
been made at different temperatures   from 0° to the boiling poi
of the liquid   As the specific gravity of a liquid varies with t
temperature, a uniform standard is essential, and all recent specific
tea quote specific gravities at 15°, compared with water at t
same temperature

Refractive Index   As the refractive power is susceptible of accu
ate measurement by means of instruments such as the Abbé refract
meter, it forms a useful guide to the identification of a solvent a
determination of its purity.   The refractive index in the case of
mixture of two organic liquids is in general the mean of those of
constituents, and it forms a means for the rapid estimation of t
proportions of a mixture of two solvents, such as white spirit an
turpentine, which differ widely in refractive power.[6]

The refractive power of a liquid varies for light of different wav
length   and also with the temperature; it is therefore essential
have these constant for accurate comparison.   The usual standa
adopted is to take the reading against the D line of the spectru
at 20°.

Distillation Range.   The wide variation in the figures given f
the same solvent in different publications is due, not only to actu
variations in the samples, but in the manner in which the distillati
is carried out.

Wide variations in the temperatures recorded for the sar
sample are possible according to the method of conducting the te
Illingworth has shown [7] that the main factors of variation are : —

(*a*) The type of apparatus used.

(*b*) The rate at which distillation is conducted.

(*c*) The position and type of the thermometer.

(*d*) The barometric pressure.

Wide variations are also possible according to different methods of working. A variation of several degrees is possible in the initial boiling point, for example, according to whether it is taken to be the reading of the thermometer (*a*) when the vapour first reaches the bulb, (*b*) when the first drop falls from the side arm of the flask, (*c*) when the first drop falls from the condenser.

For comparative results it is recognised that the test must be carried out under accurately standardised conditions. The B.E.S.A. specification for this purpose [8] is applicable to all volatile solvents. It defines the dimensions of the flask and the construction of the apparatus in detail. The range of the thermometer is not specified, but a correction is given for variation caused by the exposed thermometer stem and barometric pressure. The initial boiling point is taken as the temperature *at which the first drop falls into the receiver.*

The method adopted by the I.P.T.[9] is prescribed for volatile petroleum distillates only. The apparatus is identical with the B.E.S.A., with the exception that the thermometer is more closely specified and that the bulb is covered with a uniform layer of cotton wool. No corrections for barometric pressure or exposed thermometer stem are applied. The initial boiling point is defined as the temperature *when the first drop of liquid falls from the side arm of the flask.*

In the case of a material, such as white spirit, which comes under both the above specifications, considerable variation in the result is possible according to which is used, particularly if the thermometer chosen in the first case has a short range more accurately readable than the 0—300 range specified in the second. There is no apparent reason why one uniform method should not be agreed upon by all authorities.

In the United States the standard method of distillation is that specified by the American Society for Testing Materials [10] and adopted by U.S. Bur. Stand.[11] The English apparatus is practically identical with this, but a much shorter range thermometer is specified than that of the I.P.T., graduated from 145° to 200°. The initial boiling point is defined as the temperature at which the first drop falls from the end of the condenser. Readings are taken every 10

degrees, and the end-point is defined as when the last drop vaporised.

Evaporation and Volatility. Frequent reference has already bee made to this fundamental property of volatile solvents. In selec ing a solvent for some particular purpose consideration must l given to (*a*) the rate, (*b*) the uniformity, (*c*) the completeness o evaporation, or freedom from residue.

Whilst the rate of evaporation is generally considered to l proportional to the boiling point, the term " high boiler " ofte being used to signify a solvent which evaporates slowly, it must l borne in mind that this is only true within limits. In solvents o the same type, such as the different petroleum distillates, the boilin range is a guide to the rate of evaporation. But this does not hol with solvents of different types, because the real factors which gover evaporation are the specific heat of the substance and the latent hea of evaporation, which differ widely in different classes of compound Thus, to take an extreme case, tetrachlorethane with a boiling poin of 144° has a considerably quicker rate of evaporation than wate with a boiling point of 100°.

Connected with this is the fact that the evaporation of a liqui involves considerable absorption of heat for the conversion of th liquid into the gaseous phase. Rapid evaporation consequently results in a considerable lowering of temperature, so much so tha extremely volatile liquids, such as ether and chloroform, are em ployed as freezing agents. This lowering of temperature occurs witl all evaporation, but is greater in proportion to the rapidity of th evaporation.

H. A. Gardner [12] has measured the reduction of temperature caused by the evaporation of various solvents and published the results in a series of charts from which the following figures are abstracted as an illustration.

Lowering of temperature produced by evaporation of differen solvents under the same conditions for two minutes :

Acetone .	11·0°
Ethyl acetate .	5·9
Benzol .	5·3
Amyl acetate .	1·0
Butyl acetate .	0·6

Blushing. A practical effect of this is that the rapid evaporation of a highly volatile solvent cools the surrounding air to such ar

extent as to bring it below the dew point and cause the deposition of the moisture in it. When this occurs in the evaporation of solvents from varnish and lacquer films the deposited moisture causes a milky appearance, technically known as " blushing," due to precipitation of the resin by reaction with the water. On this account solvents are included in the composition of the varnish which evaporate so slowly that they allow this deposited water to evaporate after the volatile solvent has disappeared and redissolve the resins to restore the continuity of the film before they in turn evaporate.

Inflammability.—The great majority of volatile solvents are readily inflammable, and generally speaking the degree of inflammability, that is, the readiness with which the vapour will ignite, is inversely proportional to the boiling point in the case of hydrocarbons, and derivatives containing carbon hydrogen and oxygen.

The inflammability is, however, affected considerably by the degree of saturation and the number of oxygen and hydrogen atoms in the molecule. It has already been made evident that the introduction of chlorine reduces the inflammability, whilst the introduction of sulphur increases it.

Whilst the inflammability of a solvent has little bearing on its technical value, it is of great practical importance from the point of view of fire risk.

Flash Point. For practical purposes the relative inflammability is indicated by the temperature at which the vapour given off by the liquid will just ignite if exposed to a flame. The standard instrument for flash-point determination is the Abel apparatus. (For a full description of construction and use see " Standard Methods of Testing Petroleum," p. 18.)

A liquid is generally regarded as inflammable when the flash point is below 150° F. When the flash point lies within the limits reached by atmospheric temperature in summer it is classed as " highly inflammable." A further distinction might well be made for those solvents of exceptional inflammability which flash below 40° F. The thermometer usually supplied with the Abel instrument is only graduated to this point, and the determination of lower flash points necessitates a special thermometer, also the use of freezing mixtures to cool the liquid to below its flash point. For practical purposes there is no value in determining the exact figure in such cases the knowledge that the flash point is below 40° F. is sufficient. In the table given in the Appendix such extremely low flash points

10

are marked L (the value being given in Centigrade where it could be determined).

Although the flash point gives a general indication of inflammability, liquids of the same flash point are not always equal in fire and explosion risk, which depends also on the heat of combustion. In some exceptional cases, notably dichlorethylene, a low flash point is therefore found with a liquid which burns with such a cool flame as to present no serious risk.

Regulations. The Petroleum Acts of 1871 to 1881 class as " highly inflammable " all petroleum products which flash below 73° F. and prescribe regulations for their storage and transport. Storage in bulk is subject to licence by the local authority, in order to ensure that adequate precautions are taken against risk of fire and explosion. The Regulations made under these Acts are generally applied to the storage of other low flash solvents. Regulations for the transport of inflammable liquids in ships are issued by the Board of Trade. The general regulation governing all inflammable liquids is that the name of the substance and the flash point, or a statement that the flash point is guaranteed to be above 110° F., must be clearly marked on the package. Special instructions are given for the packing and storage of certain solvents, such as acetone, alcohols, carbon bisulphide, ethane and ethylene chlorides, petroleum spirit and turpentine. In the United States, a flash point below 30° C. (86° F.) is regarded as " highly inflammable."

Storage and Recovery. The chief points to be considered in the storage of solvents in addition to guarding against fire risk are (1) action on the container, (2) loss by evaporation. Some solvents, notably turpentines and some of the hydrocarbon chlorides, corrode iron or steel containers and must be stored in tin- or lead-lined tanks. Loss by evaporation is reduced to a minimum by designing the storage so that the tanks are not exposed to direct sunlight or other source of heat. Absorption of heat through the surface of a tank and consequent rise in temperature of the contents is reduced to a minimum by coating it with white paint of great opacity, owing to the well recognised fact, often lost sight of in industrial practice, that the more nearly a surface approaches to pure white the less the proportion of heat that falls on it is absorbed.

The recovery of solvents after evaporation is only an economical proposition where large quantities are evaporated in a confined space. In most operations of the paint industries the methods of application do not admit of efficient recovery of the solvents employed, but in the rubber industries, and particularly in extraction processes,

degreasing, etc., solvent recovery is an established practice. Several methods of recovery are used, namely :—

> Absorption by solids, such as activated charcoal and silica gel.
>
> Direct condensation at constant pressure.
>
> Condensation by spraying with water.
>
> Absorption by liquids.

C. S. Robinson has published a full account [14] of these methods and the principles on which they are based.

Physiological Action.—In the broadest sense all vapours are poisonous to human beings, as their presence in the air we breathe reduces the proportion of oxygen and interferes with the proper action of the lungs, causing asphyxiation. Even a purely inert gas like nitrogen or carbon dioxide, normally breathed in small quantity, causes asphyxiation if present in high concentration. If a solvent is used in a confined or unventilated space the headache and lassitude which are the first symptoms of insufficient oxygen inevitably become apparent after a short time. If the vapours of solvents were chemically inert this would be the only result, but in practically every case they have a more positive action on the system. The majority act, in addition, either as intoxicants or anaesthetics. When an intoxicant vapour is breathed into the lungs it is absorbed into the blood and carried to the brain, where it stimulates the brain-cells, causing exhilaration followed by depression. An anaesthetic vapour acts on the nervous system, causing fainting and, on prolonged exposure, death. A few solvents have a more virulent effect on the system, their absorption resulting in specific disease.

The *petroleum hydrocarbons*, on account of their chemical inertness, are, as a group, the least toxic in their action; they act, however, as mild intoxicants and anaesthetics, their activity being, broadly speaking, in proportion to their volatility. Thus benzine is more toxic in its action than white spirit. Dr. Alice Hamilton [15] cites cases of poisoning from petroleum ether and petrol some of which showed anaesthesia and others a similarity to alcoholic intoxication. The general experience in the use of white spirit is that it has no further ill effects than the temporary headache associated with lack of proper ventilation, and that workers soon acquire immunity.

The *Coal-tar group* of solvents vary considerably in their toxic properties according to their degree of unsaturation and consequent chemical activity. Benzene is actively toxic. The medical evidence

is conflicting as to whether its action is most pronounced when pu
or in mixtures such as benzol. In addition to general action on tl
nervous system, it is absorbed into the blood and attacks the wal
of the arteries, rendering them porous and causing hæmorrhage,
which is frequently fatal. Several cases of benzol poisoning are cite
by Sir Thomas Legge.[17] The higher homologues of benzene do no
show such marked toxicity toluene and xylene are comparative
harmless.

One would expect the naphthalene hydrides to be even less toxi
no extensive reports are available, but an investigation made by tl
Ministry of Health in Germany bears out the expectation tha
tetralin, and still more dekalin, would be practically non-toxi

The toxicity of the *Turpentine group* has been the subject of con
siderable controversy in recent years. Armstrong,[18] Goadby [19] an
Oliver [20] have claimed that much of the sickness attributed to lea
poisoning is attributable to turpentine, but this suggestion wa
rejected by the Home Office inquiry after examination.[21] Tha
turpentine vapour has a distinct toxic effect, causing headache
nausea and depression, is well established, and in some cases it act
on the kidneys, causing nephritis, which may be confused with lea
poisoning. The author has experienced two cases where men hav
been certified as suffering from lead poisoning where no lead pigmer
had been handled. The importance of such cases has been exagge
ated, however, and the general experience of painters is that it
effects are temporary and that workers soon acquire immunity.

The *Alcohol group* are characteristically intoxicant in the
action. The effect of methanol is greater than that of alcoho
because it is not so readily oxidised and remains in the systen
having a marked cumulative action.[22] In severe cases it caus
blindness, and it has been called the most deadly poison used in dail
commerce.[23]

Butanol and amyl alcohol have a more pronounced immediat
effect, causing intense irritation of the throat and headache, but th
permanent effect is not so great.

The *Ketones* act as comparatively mild intoxicants and have n
serious effect. Ether is a pronounced anæsthetic in its propertie
The *Esters*, and particularly amyl acetate, have a bad reputatior
but according to medical authorities this is not justified, as they hav
no serious toxic action. Dr. Alice Hamilton [24] considers that th
overpowering smell of amyl acetate is largely responsible for it
supposed toxicity.

Chlorine derivatives are all strongly anæsthetic in character an

require to be used with caution. Dichlorethylene, in addition, acts on the skin, causing dermatitis.

Tetrachlorethane is the most toxic member of this group, having a specific effect on the blood and on the liver-cells which results in jaundice.[25]

Carbon disulphide is a pronounced intoxicant and produces very varied effects. It has been responsible for numerous cases of sickness in the rubber industry.[26]

, The apparent toxic effects of solvents is influenced considerably by the odour. Prolonged exposure to a powerful smell increases the distress experienced out of all proportion to the actual toxic effect.

Toxic effect varies enormously with different individuals. Thus whilst some people are rendered ill by the slightest smell of turpentine, others scarcely feel any discomfort.

This applies to all cases—the author came across several instances during the war of exposure to poison gases, without ill effects, in concentration which would in general prove fatal. In most cases also repeated exposure to the fumes from a solvent, as in the case of daily work, soon develops immunity to moderate concentration. The general safe rule is to provide the most efficient ventilation, when serious results from toxicity will be avoided. In this connection it should be remembered that the vapours from all these solvents are heavier than air, and therefore the ventilation is most efficient if the current is downwards, not upwards.

The Action of Organic Solvents.—A great deal of work remains to be done before we can be said to understand fully the constitution of solutions of organic substances such as resins or waxes in organic solvents. It is, however, fairly well established that they are more in the nature of colloidal suspensions than true solutions. Van Schaack, for instance, has pointed out that nitrocellulose in acetone or amyl acetate is not a true solution, because some of the cellulose can be filtered out.[27]

The solution of polymerised oils and synthetic resins are well-known cases where a slight change in physical conditions will cause a complete separation from the solvent, indicating that no phenomenon such as ionisation has taken place, the action of the solvent being only to break up the substance into particles small enough to be invisible. In some cases the particles are just on the border-line of visibility, as in the case of a solution of damar in turpentine, which is normally slightly opalescent, but can be obtained as a perfectly clear solution if prepared in the cold with special

precautions. On warming such a clear solution, it becomes opale
cent, suggesting that the particles in the pseudo solution have forme
agglomerates of visible dimensions. Tixier [28] has gone so far as t
suggest that in the case of the solution of resins it is not the resi
that dissolves in the solvent, but the solvent in the resin, and poin
out in evidence of this that when separation of resin occurs from
mixture of oil and resin a homogeneous solution can be obtained b
adding more resin. A. A. Drummond [29] has published some sug
gestive investigations on the action of solvents on synthetic resin
Space does not, however, admit of more than a brief reference t
this complex question, sufficient to indicate the need for furthe
systematic research.

Viscosity.—The principal function of a volatile solvent in th
preparation of paint, varnish, and similar preparations is to reduc
the mixture of solids and non-volatile mediums to a consistenc
suitable for application. The viscosity of the solvent itself is there
fore of considerable practical importance, because the lower i
viscosity the less of it will be required to thin a paint to the san
degree. Although this is generally recognised, and a considerab
amount has been written as to the relative " thinning powers " c
different solvents, such as turpentine and white spirit, very litt
precise information has been published as to the action of solvents i
this direction, based on viscosity determinations.

Miscibility.—The capabilities of two different solvents to mi.
or be mutually soluble, is dependent upon the interfacial tension, *i.e*
the difference between the surface tension, or mutual attractic
between the molecules, of the respective liquids. If this differenc
is great, the molecules of each liquid will draw together in preferenc
to dispersing amongst those of the other liquid, and the two liquic
will separate. If it is small, the molecules of one liquid remai
dispersed among those of the other and the two liquids form
homogeneous mixture. Several cases have been mentioned in th
preceding chapters where the addition of a third liquid, the surfac
tension of which is intermediate between that of two immiscibl
liquids, will cause mutual solution—the addition of a small quantit
of butyl alcohol or methyl acetate, for example, results in th
miscibility of white spirit and alcohol.

In general, substances nearly alike in properties and constitutio
are completely miscible, and imperfect miscibility is due to deviatic
from the normal.[30]

The great majority of volatile solvents are mutually soluble an
non-miscible with inorganic liquids such as water. The only organ

solvents which are miscible with water in all proportions are the lower alcohols (methyl, ethyl and propyl) and the lower ketones. The higher alcohols and the acetic esters of lower alcohols have a partial solubility in water and are miscible with hydrocarbons. Acetone proves an exception to the general rule in being miscible in all proportions with both water and all other organic liquids.

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APPENDIX

SUMMARY OF THE PRINCIPAL SOLVENTS AND THEIR CHIEF PROPERTIES

* FLASH POINTS are given in both Fahrenheit and Centigrade degrees for convenience.
  L signifies that the substance flashes below 40° F.
  H signifies that the flash point is so high that the substance may be regarded as non-inflammable.
  Flash points in brackets are abnormal in not indicating inflammability.
† Solubility in water is given in volumes per cent.
  I indicates that the solubility is slight (below 1 per cent.).
  M indicates that the substance is miscible with water in all proportions.

Substance.	Formula.	Boiling range °C.	Flash point.* °F.	°C.	Specific gravity at 15° C.	Refractive index at 20° C.	Solubility in water.†
I. Petroleum Hydrocarbons.							
Pentane	C_5H_{12}	36	L		0·625	1·365	I
Hexane	C_6H_{14}	69	L		0·658	1·375	I
Heptane	C_7H_{16}	98	L		0·712	1·386	I
Petroleum ether	Indefinite	40—60	L		0·670	1·37—1·39	I
Petrol	,,	70—175	L		0·720—0·750	1·37—1·45	I
Petroleum spirit	,,	60—100	L		0·670—0·700	1·38—1·44	I
Benzine	,,	60—120	L		0·650—0·730	1·38—1·44	I
White spirit	,,	140—220	75—100	24—38	0·760—0·810	1·41—1·44	I
Shale spirit	,,	65—100	60—70	15—21	0·718—0·730	Variable	I
II. Coal-tar Hydrocarbons.							
Coal-tar naphtha	Indefinite	80—170	L		0·9	Variable	I
Benzol	,,	70—130	L		0·865—0·900	1·5	I
Solvent naphtha, light	,,	130—170	70—73	21—23	0·865—0·875	1·5	I
,, heavy	,,	160—190	75—100	24—38	0·880—0·910	1·496	I
Benzene	C_6H_6	80	L	−8	0·884	1·501	I
Toluene	$C_6H_5 \cdot CH_3$	111	45	7	0·851	1·496	I
Xylene (meta)	$C_6H_4 \cdot (CH_3)_2$	139	70	21	0·868	1·499	I
Xylol	Indefinite	135—140	86	30	0·865	1·499	I
Cyclohexane	C_6H_{12}	81	L		0·790	1·426—1·429	I
Tetralin	$C_{10}H_{12}$	205	172	78	0·980	1·540	I

SUMMARY OF THE PRINCIPAL SOLVENTS AND THEIR CHIEF PROPERTIES—*continued.*

Substance.	Formula.	Boiling range °C.	Flash point.*		Specific gravity at 15° C.	Refractive index at 20° C.	Solubility in water.†
			°F.	°C.			
III. *Turpentines.*							
Turpentine, American ...	C₁₀H₁₆	150—180	90—95	32—35	0·860—0·880	1·466—1·478	I
" French ...	C₁₀H₁₆	155—170	86—90	30—32	0·857—0·872	1·466—1·478	I
" Indian ...	C₁₀H₁₆	155—190	99	37	0·865—0·880	1·481	I
Wood turpentine, American	C₁₀H₁₆	150—170	93—97	34—36	0·860—0·863	1·467—1·469	I
" Russian.	Indefinite	160—180	95—100	35—38	0·862—0·875	1·476	I
Tar spirit ...	Indefinite	125—270	72—74	22—23	0·9—1·0	Variable	I
Pine oil ...	"	190—218	95—105	35—40	0·93—0·95	1·480—1·483	I
Terpineol ...	C₁₀H₁₇·OH	210—219	116	47	0·923—0·940	1·481	I
Hydroterpin	C₁₀H₁₈	179—195			0·879	1·473	I
Rosin spirit ...	Indefinite	115—120	97—102	36—39	0·856—0·883	Variable	I
IV. *Alcohols.*							
Methyl alcohol ...	CH₃OH	66	59	15	0·796	1·332	M
Absolute alcohol ...	C₂H₅OH	78	53	12	0·79	1·367	M
Industrial spirit ...	Impure	76—79	64	18	0·815—0·820	1·362	M
Propyl alcohol, normal ...	C₃H₇·OH	97			0·804	1·386	M
" iso ...	C₃H₇·OH	79—81			0·790	1·381	M
Butyl alcohol ...	C₄H₉·OH	110—118	97	36	0·810	1·396	8
Amyl alcohol ...	C₅H₁₁·OH	121—131	111	44	0·825	1·408	3
Di-acetone alcohol ...	C₂H₅·CO·(CH₃)₂·COH	163	L		0·910—0·930		M
Benzyl alcohol ...	C₆H₅·CH₂OH	206	154	68	1·051	1·468	I
Hexalin ...	C₆H₁₁OH	160	154	68	0·945	1·463	I
Methyl-hexalin	C₆H₁₀·CH₃·OH	170—180			0·930		I

SUMMARY OF THE PRINCIPAL SOLVENTS AND THEIR CHIEF PROPERTIES—*continued.*

Substance.	Formula.	Boiling range °C.	Flash point* °F.	Flash point* °C.	Specific gravity at 15° C.	Refractive index at 20° C.	Solubility in water.†
V. Ketones and Ethers.							
Acetone	(CH₃)₂CO	56	L		0·792—0·799	1·358	M
Methyl ethyl ketone	CH₃·CO·C₂H₅	70—83	L		0·810	1·379	M
Methyl acetone	Indefinite	50—70	L		0·840—0·850	1·35—1·36	M
Cyclohexanone	C₆H₁₀·O	135—165	145	64	0·930—0·950	1·443	9
Ethyl ether	(C₂H₅)₂O	35	L		0·719—0·735	1·356	
VI. Esters.							
Methyl acetate	CH₃COO·CH₃	53—59	L	−6	0·923—0·930	1·361	50
Ethyl acetate	CH₃COO·C₂H₅	70—83	L	−3	0·893—0·895	1·373	8—16
Butyl acetate	CH₃COO·C₄H₉	107—135	76	24	0·870—0·875	1·404	1
Amyl acetate	CH₃COO·C₅H₁₁	125—150	77	25	0·870—0·875	1·404	0·5
Hexalin acetate	CH₃COO·C₆H₁₀·OH	165—180	147	64	0·965—0·970	1·438	I
Ethyl lactate	CH₃·CHOH·COO·C₂H₅	145—159	117	47	1·038		
VII. Chlorine Derivatives.							
Methylene chloride	CH₂Cl₂	42	(100)		1·328	1·449	0·8
Chloroform	CHCl₃	61	H		1·48—1·49	1·461	I
Carbon tetrachloride	CCl₄	77	H		1·629		I
Dichlorethylene	C₂H₂Cl₂	48—60	(36)		1·273	1·479	I
Trichlorethylene	C₂HCl₃	87	H		1·471	1·505	I
Perchlorethylene	C₂Cl₄	121	H		1·624	1·501	I
Tetrachlorethane	C₂H₂Cl₄	147	H		1·601	1·502	I
Pentachlorethane	C₂HCl₅	159	H		1·655	1·527	I
Monochlorbenzene	C₆H₅Cl	132	56	13	1·11		I
Dichlorbenzene	C₆H₄Cl₂	172	62	17	1·35		
Dichlorhydrin	CH₂Cl·CH·OH·CH₂Cl	173	H		1·37		10
Epichlorhydrin	CH₂Cl·CH·CH₂	117	H		1·194		
VIII.							
Carbon bisulphide	CS₂	48					

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